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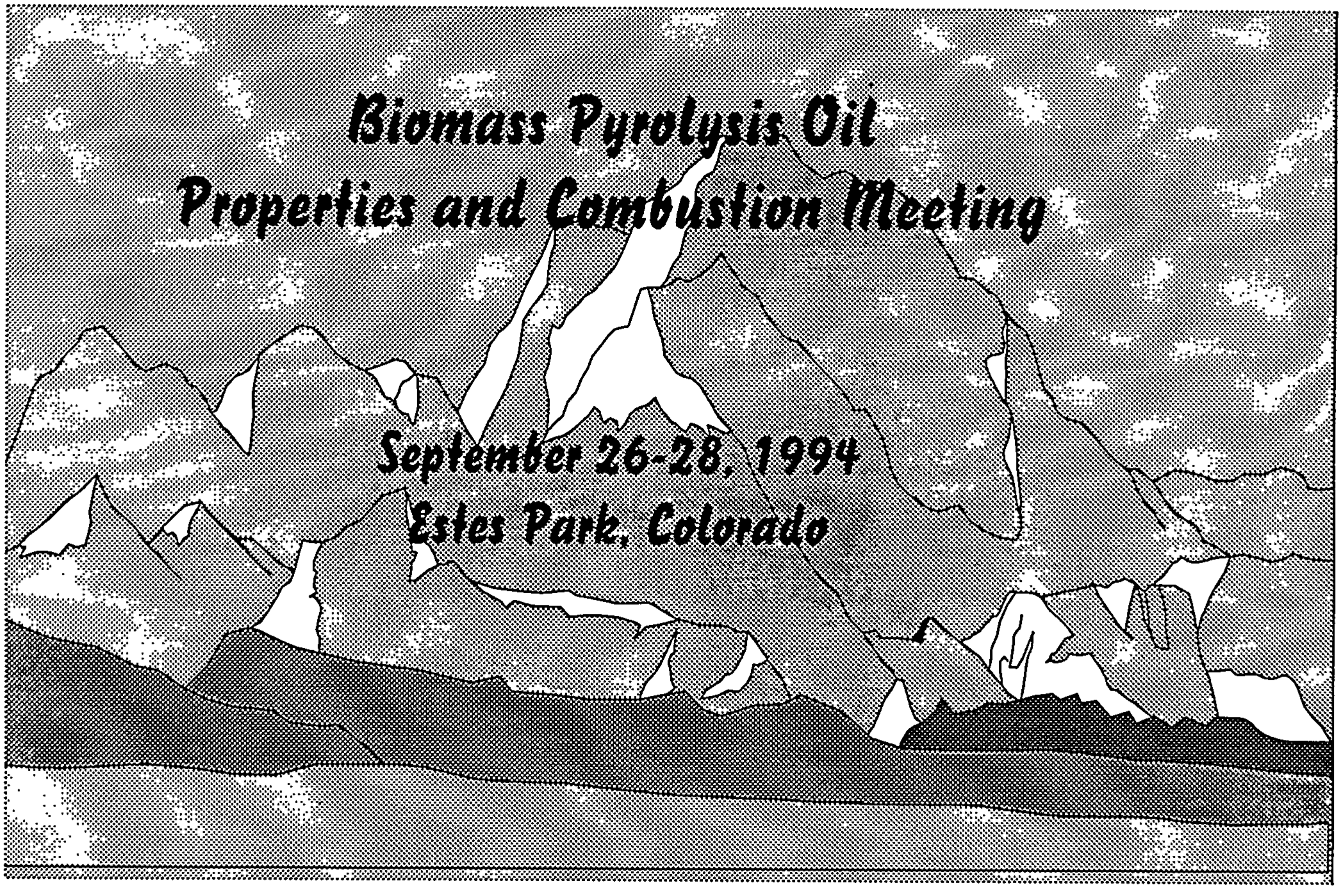

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Preface

The increasing scale-up of fast pyrolysis in North America and Europe, as well as the exploration and expansion of markets for the energy use of biocrude oils that now needs to take place, suggested that it was timely to convene an international meeting on the properties and combustion behavior of these oils. A common understanding of the state-of-the-art and technical and other challenges which need to be met during the commercialization of biocrude fuel use, can be achieved.

The technical issues and understanding of combustion of these oils are rapidly being advanced through R&D in the United States, Canada, Europe and Scandinavia. It is obvious that for the maximum economic impact of biocrude, it will be necessary to have a common set of specifications so that oils can be used interchangeably with engines and combustors which require minimal modification to use these renewable fuels. Fundamental and applied studies being pursued in several countries are brought together in this workshop so that we can arrive at common strategies. In this way, both the science and the commercialization are advanced to the benefit of all, without detracting from the competitive development of both the technology and its applications.

This United States-Canada-Finland collaboration has led to the two and one half day specialists meeting at which the technical basis for advances in biocrude development is discussed. The goal is to arrive at a common agenda on issues that cross national boundaries in this area. Examples of agenda items are combustion phenomena, the behavior of trace components of the oil (N, alkali metals), the formation of NO_x in combustion, the need for common standards and environmental safety and health issues in the handling, storage and transportation of biocrudes.

Thomas A. Milne

Thomas A. Milne
for The Technical Committee

Biomass Pyrolysis Oil Properties and Combustion

Co sponsored by the U.S. DOE, NREL, Natural Resources Canada (NRCan) and VTT Energy, Finland

FINAL PROGRAM

Saturday and Sunday, September 24, 25, 1994

Hikes in Rocky Mountain National Park - Organized by Mike Antal and John Scahill	

Sunday, September 25, 1994

TIME	FUNCTION
5:00 - 7:00pm	Dinner served in cafeteria
7:00-10:00pm	Dessert Reception and Registration

MONDAY, SEPTEMBER 26, 1994

MORNING - SESSION #1	
TIME	**FUNCTION**
7:00 - 8:00	Breakfast served in cafeteria
7:00 - 8:30	Registration
8:30-8:45	Welcome - Industrial Technology Division Welcome - Bill Marshall, Deputy Director for Operations, NREL
8:45 - 9:15	**Introduction and Overview of National Biomass Power Programs** Yrjo Solantausta (VTT); Ralph Overend (NREL), and Ed Hogan (NRCan)
	Fundamentals Discussion Leader: Don Scott University of Waterloo
9:15-9:45	*Cellulose Pyrolysis Kinetics: The Current State of Knowledge* Michael Antal (U. of Hawaii)
9:45-10:15	*Chemical Analysis of Biomass Fast Pyrolysis Oils* Doug Elliott (PNL)
10:15-10:45	Coffee Break
10:45-11:15	*Properties and Characteristics of Ensyn Bio-Oil* Narendra Bakhshi (U of Saskatchewan)
11:15-12:15	*Storage of Biomass Pyrolysis Oils* Stefan Czernik (NREL) *Inorganic Compounds in Biomass Feedstocks: Their Role in Char Formation and Effect on the Quality of Fast Pyrolysis Oils* Foster Agblevor (NREL) *Hot Gas Filtration to Remove Char from Pyrolysis Vapors Produced in the Vortex Reactor at NREL* Jim Diebold (NREL)
12:15-1:00	Lunch served in cafeteria
1:00 - 5:00	Afternoon - Free time, ad hoc group discussions
1:15 - 4:15	Park Service Walking Tour. Meet at Main Lodge at 1:15.
5:00 - 6:30	Dinner served in cafeteria
EVENING - SESSION #2 - Discussion Leader: Don Huffman (Ensyn)	
	Fast Pyrolysis Oil Production and Economics -
7:00-7:30	*Engineering Developments in Fast Pyrolysis for Bio-Oils* - Tony Bridgwater (Aston University)
7:30-8:00	*Pyrolysis Oil Economics - Issues and Impacts* Cathy Gregoire (NREL)
8:00-8:30	*Flash Pyrolysis of Biomass in a Circulating Fluidized Bed Reactor* - Ionnis Boukis (CRES)
8:30-9:00	*The Production and Handling of WFPP Bio-Oil and its Implications for Combustion* - Angel Cuevas (Union Fenosa)
	Environmental Safety and Health and Fuel Specifications and Standards -
9:00-9:30	*Environmental Considerations in the Production and Use of Biomass Fast Pyrolysis Oils* - Doug Elliott (PNL)
9:30-10:00	*Results of Toxicological Testing of Whole Wood Oils Derived from the Fast Pyrolysis of Biomass* - David Gratson (NREL)

TUESDAY, SEPTEMBER 27, 1994

MORNING - SESSION #3 Discussion Leader: Don Hardesty (Sandia)

TIME	**FUNCTION**
7:00 - 8:00	Breakfast served in cafeteria
	Combustion in Boilers and Furnaces
8:30 - 9:00	*Specifications for Liquid Fuels in Boilers* (tutorial) - Scott Drennan (Coen Company
9:00 - 9:30	*Sprays and Spray Combustion* (tutorial) - John Daily (U. of Colorado)
9:30 - 10:00	*Formation of Nitrogen Oxides in Combustion Processes* (tutorial) - Mel Branch (U. of Colorado)
10:00 - 10:30	Coffee Break
10:30 - 11:00	*Single-Droplet Combustion of Biomass Pyrolysis Oils* Judy Wornat (Princeton)
11:00 - 11:30	*Baseline NO_x Emissions During Combustion of Wood - Derived Pyrolysis Oils* - Larry Baxter (Sandia)
11:30 - 12:00	*Combustion Characterization of Wood Derived Flash Pyrolysis Oils in Industrial-Scale Turbulent Diffusion Flames* - Alan Shihadeh (MIT)
12:00-12:30	*Alkali, Chlorine, SO_x and NO_x Release During Combustion of Pyrolysis Oils and Chars* David Dayton (NREL)
12:30 - 1:00	Lunch served in cafeteria
1:00 - 5:00	Afternoon - Free time, ad hoc group discussions, park visits on your own
5:00 - 6:30	Dinner served in cafeteria

EVENING - SESSION #4 Discussion Leader: Yrjö Solantausta (VTT)

	Combustion in Boilers and Furnaces (cont.) -
7:00 - 7:30	*Applied Bio-Oil Combustion* - Barry Freel (Ensyn) (Presented by Don Huffman)
7:30- 8:00	*Flash Pyrolysis Fuel Oil* - Steven Gust (NESTE)
8:00 - 8:30	*Bio-Oil Combustion Tests at ENEL* - Carlo Rossi (ENEL)
8:30 - 9:00	*Economic Development Through Biomass Systems Intergration* - Donna Johnson (Meetech)
	Integration of Bio-Oils into Utilities - Jerry Lonergan (Kansas Elec. Util Res. Program) (Abstract and Paper only.)
9:00 - 9:30	Discussion

WEDNESDAY, SEPTEMBER 28, 1994

MORNING - SESSION #5 Discussion Leader: Ralph Overend (NREL)	
TIME	**FUNCTION**
7:00 - 8:00	Breakfast served in cafeteria
	Combustion in Internal Combustion Engines
8:30 - 9:00	*Comparative Study of Various Physical and Chemical Aspects of Pyrolysis Bio-Oils Versus Conventional Fuels Regarding their use in Engines* Jesus Casanova (U. of Polyt, Madrid)
9:00 - 9:30	*Use of Pyrolysis Oil as a Fuel in a Diesel Power Plant* Yrjo Solantausta(VTT)
	Combustion in Turbines
9:30 - 10:00	*Fuel-Specification Considerations for Biomass Liquids* (tutorial) Cliff Moses (SWRI)
10:00 - 10:30	Coffee Break
10:30 - 11:00	*Firing Fast Pyrolysis Oil in Turbines* R. Andrews (Hawker-Siddeley)
	Conclusion
11:00 - 12:00	*RD &D Needs and Plans, Wrap-up* - Ralph Overend (NREL)
12:00-1:00	Lunch served in cafeteria
1:00	ADJOURN

Table of Contents

Biomass Pyrolysis Oil Properties and Combustion
September 24 – 28, 1994
Estes Park, Colorado

Finnish Endeavours in the Field of Biomass Pyrolysis

Kai Sipilä, Yrjö Solantausta
VTT Energy
P.O. Box 1601, FIN-02044 Espoo, Finland

Two R&D pathways related to biomass pyrolysis are being explored in Finland: Neste Oy is studying the replacement of fuel oil with flash pyrolysis oil, and Wärtsilä Diesel International Ltd. and Vapo Oy are exploring possibilities for using pyrolysis oil as diesel power plant fuel. Both of these ventures are supported by research at VTT Energy. In addition to the contributions of the companies themselves, the Ministry of Trade and Industry has been funding the work.

Neste is evaluating the supplementation of certain market segments, light fuel oils for heating large premises, with a biomass derived alternative. Pellet stoker boilers and grate boilers would be the more traditional solutions. Although the economics presently are uncertain, carbon tax or other related proposed measures may improve the competiveness. In addition to laboratory work on pyrolysis oil properties, Neste is conducting experiments in test boilers.

Extremely low-quality (high viscosity, high levels of metals) oils can be employed as fuels in medium and low speed diesel engines. One of the pioneers of the field, Wärtsilä, is developing a system that would tolerate such pyrolysis oils. Together with Vapo, a Finnish fuel producer, and VTT, an advanced biomass power plant concept is being developed.

VTT is carrying out supporting experimental work for these efforts. A 4-cylinder VALMET diesel engine has been modified for pilot-injection. The engine has been operated with pyrolysis oil for short periods. Work has also been carried out on both basic and applied aspects of pyrolysis oil production and oil analysis. Solids removal has also been studied. Experimental work on pyrolysis will be increased in volume during 1995.

U.S. DEPARTMENT OF ENERGY PYROLYSIS RELATED ACTIVITIES

Richard Bain
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The U. S. Department of Energy (USDOE), with National Renewable Energy Laboratory (NREL) is involved in a number of biomass pyrolysis related activities. Studies are being performed through the Office of Utility Technologies (OUT) and the Office of Transportation Technologies (OTT), both of which are part of Energy Efficiency and Renewable Energy (EE). The USDOE programs have the goal of reducing the risks associated with commercializing new technologies and feedstocks for electricity, transportation fuels. and chemicals.

Studies are being performed as part of the OUT Biomass Power Program to determine the suitability of biocrude (pyrolysis oil) as a gas turbine fuel or diesel fuel for the production of electricity. To this end investigations of biocrude and char combustion studies are being performed by Sandia National Laboratories Livermore. Technoeconomic studies are being performed for pyrolysis-combined cycle electricity production systems. Laboratory studies are being performed using ablative pyrolysis and fluid-bed reactors to determine system modifications required to produce commercially acceptable fuels. For examples, hot-gas filtration apparatus is being used to reduce the alkali level of biocrude.

OUT's Hydrogen program is supporting investigations at NREL of the pyrolysis of lignocellulosic biomass and reforming of the pyroligneous oils for the production of hydrogen. Thermodynamic modelling and technoeconomic analyses of conceptual processes have indicated that a process of this nature has the potential to be cost effective with conventional means of hydrogen production. Catalysis research has been initiated for the development of novel catalytic systems for the reforming of pyroligneous oils.

OTT's thermochemical fuels program is sponsoring research for the production of oxygenated gasoline additive based on the ablative pyrolysis of biomass. Both pilot-scale research and supportive technoeconomic studies are underway. The concept being developed involves the production of pyrolytic vapors, followed by catalytic conversion of the pyrolytic vapors to intermediate species which can be reacted with an alcohol to form mixed ethers. NREL research is concentrating on producing a suitable feed stream to a commercial ether production unit. Evaluations are also being performed to assess the suitability of biocrude as a refinery feedstock, with efforts concentrating on using biocrude as a specific unit operation additive, and not as a refinery crude.

Bioresource Technology 46 (1993) 86–93

ELECTRICITY FROM BIOMASS IN THE UNITED STATES: STATUS AND FUTURE DIRECTION

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Abstract

The biomass power industry in the United States has grown from less than 200 MW in 1979 to more than 6000 MW in 1990, primarily as a result of the Public Utilities Regulatory Policies Act of 1978. The United States Department of Energy (USDOE) is projecting installed capacity will grow to about 22 GW by the year 2010, with environmental considerations (carbon dioxide neutrality, low sulfur dioxide emissions, and low nitrogen oxides emissions) being the primary driving force. The primary conversion technologies being developed in the United States are gasification–combined cycle systems, pyrolysis oil–combined cycle systems, and advanced direct combustion systems. The USDOE program has the objective of reducing the risks associated with commercializing new technologies and feedstocks for power production. The program is divided into two areas: research and development and systems analysis. The major research and development program is in the area of hot-gas cleanup, while the systems analysis area is concentrating on gasifier scale-up and site-specific commercial feasibility studies.

Key words: Alkali deposit, biomass-to-electricity, carbon dioxide, dedicated feedstock supply systems (DFSS), direct-fired turbine, electricity, Energy Policy Act (EPACT) of 1992, gasification, gas turbine, Hawaii biomass gasification facility, hot-gas cleanup, PURPA (Public Utilities Regulatory Policies Act of 1978), pyrolysis, steam turbines, whole tree energy.

INTRODUCTION

Since 1978, the USA biomass-power industry has installed over 6 gigawatts (GW) (Rader, 1990) of grid-connected generating capacity, much of it associated with the wood and wood-products industry, which obtains more than half of its electricity and thermal energy from biomass. In comparison, coal-fired electric units in the USA account for approximately 297 GW of capacity (Energy Information Agency, 1989), or about 43% of total generating capacity. The use of biomass in 1989 was more than 3·5 exajoules (EJ), or about 4·3% of the total USA primary-energy use of about 81 EJ. More than 70% of biomass-based power is produced on a cogeneration basis. Wood-fired systems represent 88% of total capacity, followed by landfill gas at 8%, agricultural wastes at 3%, and anaerobic digesters at 1%. Biomass electric-generating capacity by state is shown in Fig. 1.

Biomass power plants use technology that is very similar to that used in coal-fired power plants. For example, biomass plants use similar steam-turbine generators and fuel-delivery systems. However, coal combustion is more mature technology, which is reflected in higher power efficiencies. Today's biomass power-plant efficiencies are typically 15–20%, and the best units have efficiencies of about 25%. Electricity costs are in the 6·5–8·5 c/kWh range. The average biomass power plant is about 20 megawatts (MW) in size, with a few dedicated wood-fired plants in the 40–50-MW size range. It is estimated that there are nearly 1000 biomass-fired plants in the USA, only a third of which offer electricity for sale. The rest are owned and operated by the paper and wood-products industries for their own use. Meanwhile, modern coal-fired power plants are larger and have efficiencies of 30–35%. Coal plants achieve higher efficiencies because coal has

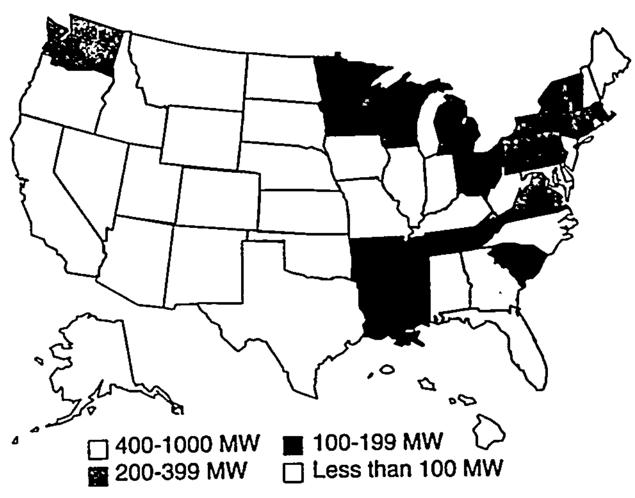

Fig. 1. Biomass-electric-generation capacity of state, 1989.

more energy density per kilogram than biomass; because biomass has a higher moisture content, resulting in a lower heating value per unit mass; and because biomass has a higher moisture content, resulting in a lower heating value per unit mass; and because economies of scale make the installation of high-efficiency systems economically feasible.

In the USA, biomass-electric-power capacity experienced dramatic growth after the Public Utilities Regulatory Policies Act (PURPA) of 1978 guaranteed small electric-power producers that utilities would purchase their surplus electricity at a price equal to the utilities avoided cost of producing electricity. From less than 200 MW in 1979, biomass-based capacity grew to about 6 GW in 1989 by using avoided-cost contracts and tax credits. In 1986, 1·84 GW of biomass-based capacity became operational, which was more than half of the 3·05 GW of biomass-based power introduced from 1980 through 1985. But, in 1989, based primarly on competitive bid contracts and without tax credits, only 0·61 GW of wood-fueled electricity capacity was introduced. In 1990, new additional capacity was only 0·25–0·30 GW.

As just stated, the growth of the biomass electric industry had slowed significantly by the end of the 1980s. Low oil and natural-gas prices, slow electrical-demand growth, and, in some areas, such as California, feedstock-supply shortages substantially undermined the commercial attractiveness of small-scale biomass plants. Other contributing factors included loss of tax credits, shifts in the implementation of PURPA toward competitive bidding, and lack of acceptance of large independent power producers. Net plant-heat rates for 25-MW plants in Pacific Gas and Electric's (PG&E) service territory in California averaged about 18% efficiency (PG&E, 1991). These units are much smaller than typical utility-owned pulverized coal-fired stations with capacities of 600–1200 MW and efficiencies greater than 34%. Fuel prices also vary widely from essentially no cost for self-generators to over $55 per dry tonne for supply-constrained markets. To remain a competitive power-generation option in the absence of tax credits or other renewable energy-production incentives, the biomass-power industry will need improvements in both the feedstock-supply system and the energy-conversion technology.

The goal of the United States Department of Energy (USDOE) Office of Conservation and Renewable Energy (CE), Biomass Power Program, with the National Renewable Energy Laboratory (NREL) as the lead-field laboratory, is to assist industry in producing low-cost electricity from sustainable biomass resources. The key to meeting this goal is the introduction of higher-efficiency technologies. Recently, in the USA, there has been a growing interest in developing advanced power-generating systems using advanced gas turbines, based primarily on analyses of Williams and Larson at Princeton (Larson, 1990) and of the USDOE (OSEC, 1992). The advanced systems have the potential for higher generation efficiencies (35–40%) and lower costs of electricity (4·5–5·5¢kWh) than conventional systems. Turbine-based systems being evaluated include open-cycle gas turbines, steam-injected gas turbines, intercooled steam-injected gas turbines, combined-cycle systems, and cogeneration systems.

The purpose of this paper is to discuss the status of the USA biomass-power industry, to discuss the rationale for the development of biomass-based electricity-generation capacity, and to outline the ongoing USDOE program to assist industry in developing new biomass-based electricity-generation capacity.

RATIONALE

There are a number of reasons why biomass is an attractive feedstock for electricity genertion in the USA. First, biomass is an indigenous and renewable resource. Like coal, it represents a secure domestic source of energy that is not subject to the price fluctuations and supply uncertainties of imported petroleum and natural gas. The use of biomass to displace imported energy affects the US balance of payments in a positive manner.

Feasibility

As discussed in the Introduction, the feasibility of using biomass to produce energy is well demonstrated in the USA, with biomass supplying more than 4% of the primary-energy demand (Douglas, 1991). The industry is characterized by small plants with low efficiencies, relying primarily on waste materials as feedstocks. As the biomass-to-electricity industry grows, it will be characterized by larger facilities of 50–150-MW capacity, with gas-turbine-based cycles, as shown in Fig. 2. This will result in higher-efficiency processes and will require reliance on dedicated biomass energy crops as feedstocks. It is important to note that the existing biomass-power industry has demonstrated that the infrastructure is available to supply feed to 20%-efficiency steam-turbine plants with up to 50-MW capacity. With the introduction of higher-efficiency plants, this same infrastructure will then be able to supply plants of 50–100-MW capacity. The larger size range is consistent with existing commercially available aeroderivative turbines. The technical development of sustainable feedstock systems has been demonstrated by the pulp and paper industry in the USA and in South America. Hence the only system component that needs to be demonstrated is the primary-biomass-conversion step to supply clean gas to the gas turbine. Other primary-conversion processes, such as the advanced direct-combustion cycle Whole Tree Energy (Ostlie, 190), have also developed to the point of large-scale demonstrations.

Environmental impacts

Biomass is lower in sulfur than are most US coals. A typical biomass will contain 0·05–0·20 wt% sulfur and

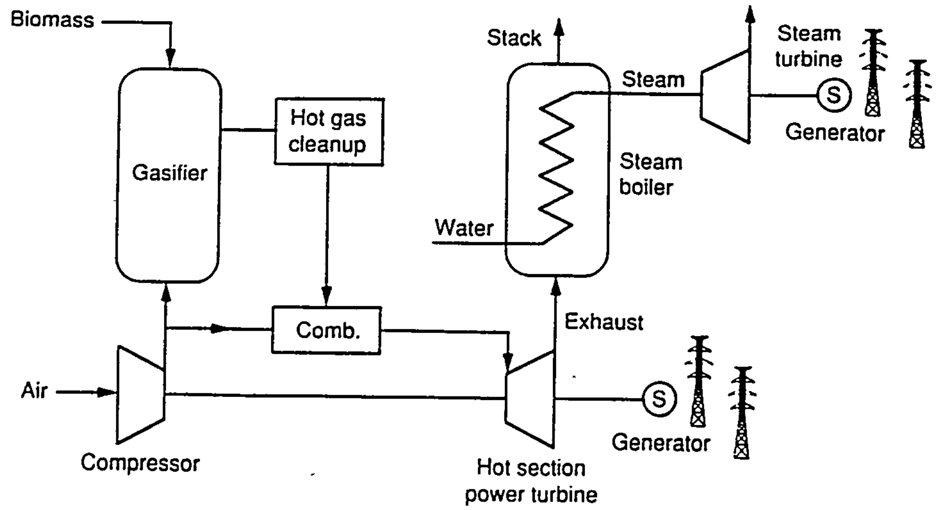

Fig. 2. Integrated gasifier combined cycle (IGCC).

have a higher heating value of about 20 000 kJ/kg. This sulfur content translates to about 51–214 mg SO_2/MJ (0·05–0·12 lb SO_2/MM Btu). The higher level is still less than the regulated limit set out in the current New Source Performance Standards (NSPS) shown in Table 1. Controlled NO_x levels from biomass plants will also be less than the levels of NSPS standards, as shown in Table 2, which gives performance guarantees for typical California biomass-power plants using the best available control technology.

The regulation of atmospheric emissions has changed dramatically with the passage of the Clean Air Act Amendments of 1990 (CAAA'90). In Title IV of CAAA'90, SO_x regulation may benefit biomass power and will be discussed. Title IV represents a major opportunity for all non-sulfur-containing fuels, including biomass-fueled facilities. The basis of this acid-rain legislation is the mandated reduction of utility SO_2 emissions by 9·1 million tonne compared with 1980 emissions by the year 2000. In addition, this title creates a special class of benefits for all renewable fuels. In the first phase of SO_2 reductions, there will be 300 000 incentive allowances for renewable energy facilities installed by utilities to achieve SO_2 reductions before they are covered by regulations in 1995. The rate has been given as 0·0018 kg/kWh multiplied by the number of kWh displaced by conservation or generated by a renewable generator. Assuming the value of an allowance to be \$552/tonne, the incentive amounts to 0·1c/kWh to the renewable facility. The Phase 1 allowances come into effect in 1995 and will be followed by a second phase in the year 2000. In this phase, all units will be subjected to the regulations and will be restricted to 1516 mg/MJ as a maximum heat-release rate. The total number of allowances issued will be 8·9 million. The tighter limits coupled with a growth in electricity demand will presumably result in an increase in the value of an allowance. This is recognized by the EPA in that it proposes a fine of \$2204/

Table 1. New source-performance standards

Source	SI units	English units
Particulates	13 mg/MJ	0·03 lb/MM Btu
SO_2[a]	517 mg/MJ	1·2 lb/MM Btu
SO_2[b]	259 mg/MJ	0·6 lb/MM Btu
NO_x	259 mg/MJ	0·6 lb/MM Btu

[a] These are based on coal units that achieved 90% reduction of emissions since 1985: the limits after the installation of cleanup systems.
[b] For coal units that have achieved 70% reduction.

tonne SO_2 for an emitter who exceeds his allowance, along with a debit of one unit from the following year's allowance to ensure that the over-all emissions pool is not increased. This high value could result in significant premiums for efficient biomass-power plants.

Biomass is a renewable resource that consumes carbon dioxide during its growing cycle, so its use for energy production contributes no net carbon dioxide to the atmosphere when the biomass is produced and consumed on a sustainable basis as part of a dedicated feedstock-supply system/energy-production system. Harvesting and burning of biomass such as old-growth forests or tropical forests on a non-sustainable basis do contribute net carbon dioxide to the atmosphere. However, in a dedicated energy system, new trees or plants are grown to replace harvested biomass, thus creating a closed-loop biomass system that theoretically produces no net carbon dioxide. In actual practice, some fossil fuels are consumed during harvesting and transportation of biomass and in the production of fertilizers; but this is small compared with the total carbon dioxide produced and consumed in the biomass-energy cycle. Furthermore, when mature old-growth forests are harvested and replanted with young trees, there is a one-time net carbon dioxide consumption-rate increase because mature trees consume about 3 tonne

Table 2. Comparison of current biomass-combustion-technology-emissions guarantees

	Pile burner	Traveling grate	Suspension-fired	CFBC	Fluid bed
Particulates mg/dry nM^3 @ 12% CO_2	206	57	53	23	229
Nitrogen oxides, mg/MJ[a]	86	50	77	35	34
Carbon monoxide, mg/MJ	129	129	65	28	60
Non-methane HCs, mg/MJ	43	17	NA	121	43
Sulfur dioxide, mg/MJ	NA	NA	NA	43	14

Ref: Hollenbacher (1992).
[a]All systems except the pile burner and the suspension burner use a non-catalytic deNO_x system.

of carbon/hectare/year, whereas new growth consumes about 10 tonne/hectare/year (Elliott, 1990).

Economic impacts

The use of biomass to produce electricity in a dedicated feedstock-supply system/electricity-generation system will provide new revenue sources to the depressed US agriculture system by providing a new market for farm production. The growing of crops, either herbaceous or woody, will provide product diversity for the farm economy. In many areas, land idled because of depressed markets or set aside through government programs can be returned to productive use. The use of certain crops, such as switchgrass in the corn belt or harvestable trees in shelter belts, may actually contribute to biodiversity, thus affecting the environment in a positive way.

A recent study performed for USDOE estimates the present and future impact of biomass-power production of the US economy (Meridian & Antares, 1992). In 1992, electrical production from biomass, primarily wood, had a net impact of $1.7 billion in personal and corporate income and represented more than 62 000 jobs. The study estimates that, in 2010, biomass electrical-generating capacity will have grown to approximately 22 GW. At this capacity level, the economic benefits are estimated to be $6.2 billion* in personal and corporate income and 238 000 jobs. These benefits will have a substantial positive benefit on rural America.

The export of higher-efficiency biomass-to-electricity technologies to developing countries is desirable. Many developing countries rely on biomass to provide much of their energy requirement. More efficient use of biomass in producing energy, both electrical and thermal, may allow developing countries to reduce petroleum imports, thus affecting their balance of payments dramatically. Although construction of new facilities will generally require infusion of foreign capital into foreign countries, more efficient energy production should reduce reliance on long-term foreign subsidies from countries such as the USA.

*This is the US billion = 10^9.

INDUSTRY PROJECTIONS

Biomass-generating capacity in the 1980s was characterized by 10–50-MW conventional steam turbines fueled by waste wood and agricultural residues. During the late 1990s, the industry is expected to undergo a significant change toward 50–150-MW state-of-the-art plants, with combined gas and steam cycles. The plants will increasingly be fueled by a system of dedicated biomass-feedstock systems providing a high-yield feedstock with consistent chemical and physical characteristics. These changes are expected to have important ramifications in the efficiency, cost of electricity, availability, and reliability of biomass-power plants. The timing for these changes will depend on the pace of R&D efforts and on the pace of changes now affecting the business environment for power producers.

On the basis of the successful execution of the R&D program described later and the successful resolution of technical and economic risks, three energy-conversion technology-development paths coupled with the developed of dedicated-feedstock-supply systems (DFSS) are expected to contribute to widespread use of biomass-power systems. These technologies are direct-combustion systems, integrated biomass-gasification-power systems, and combustion systems powered by biomass-pyrolysis fuel oils. The transition will take place gradually over the next decade, progressing from early application for direct-fired gas turbines or cofiring of biomass-pyrolysis oils with pulverized coal to repowering of existing wood-fired steam turbines with gas-turbine topping cycles, and eventually to integrated gasification combined cycles and intercooled steam-injected gas-turbine (ISTIG) power plants with DFSS.

Of the current 3·5 EJ of biomass use, less than 1 EJ is specifically used for power production (USDOE, 1991). The development and use of greatly improved forest-management and recovery techniques could allow natural forest systems to provide up to 3·2 EJ per year of wood feedstocks for power production by the year 2010. Accelerated-energy-crop R&D could allow biomass-energy farms to contribute another 6·5 EJ per year of energy for biomass power, making an estimated total of 10 EJ per year of biomass feedstock for future power production. Future widespread availability of biomass feedstocks resulting from high-productivity

energy-crop development may provide the energy resources to allow utilities and independent power producers ultimately to develop in excess of 100 GW of biomass-powered facilities. The Solar 2000 strategy promulgated by USDOE has set a goal of the installation of 4 GW of new biomass-power capacity in the USA by the year 2000 (USDOE, 1991).

Figure 3 shows the expected capacity in the US biomass-power industry given a vigorous research and development (R&D) program by USDOE and other interest parties. Over-all total capacity is expected to increase by about 4 GW by the year 2000 to 10 GW, and by another 9 GW by the year 2010, bringing the total installed capacity to about 19 GW. Through the year 2000, steam-turbine and steam-turbine-cogeneration sytems will continue to constitute the major proportion of capacity, with gas-turbine cycles contributing about 3 GW. By the year 2010, gas-turbine cycles are expected to make up in excess of 80% of installed capacity, or greater than 16 GW.

TECHNOLOGY CONSIDERATIONS

Biomass can be used as a primary-energy source or as a secondary-energy source to power gas turbines. As a primary source, biomass is used for direct combustion as a bulk fuel, as is done in most of today's biomass-power industry.

As a secondary-energy source, biomass is used to make a fuel, which can then be used to fire a gas turbine. The key issue facing researchers in this area is developing sufficiently clean fuels so that the hot section of the turbine is protected from particulate build-up and corrosion.

Direct combustion of biomass

One alternative for producing electricity from biomass in a gas turbine is direct combustion of biomass as a primary-energy source. Direct combustion usually involves reducing the biomass into fine pieces for fueling a close-coupled turbine system. In a close-coupled system, biomass is burned in a combustion chamber separated from the turbine by a filter. The USDOE is supporting development through a subcontract with Power Generating Inc., of Fort Worth, Texas, USA.

Energy Performance Systems Inc., of Minneapolis, Minnesota, USA, is developing the Whole Tree Energy (WTE) technology. The WTE process uses a pile-type three-stage combustor to burn whole trees or logs. Waste heat is used to dry the trees prior to combustion. Relatively high furnace efficiency, about 87%, and over-all power-plant-cycle efficiency of 33–36% have been projected for the WTE process. The developer states that this process is feasible for 25–400-MW plants.

Biomass-derived fuels for gas turbines

Another alternative is to produce a fuel from biomass as a secondary energy source. The USDOE Biomass Power Program and the biomass-power industry are developing several processes to produce clean biomass-derived fuels, which can take either gaseous or liquid form. Gaseous fuels consist of low- and medium-calorific-value gases; the liquid is a primary-pyrolysis oil called biocrude.

Using biomass-derived fuels in gas turbines has several potential advantages over the direct combustion of biomass. Such fuels not only have higher efficiency, they also burn much more cleanly than does bulk biomass. These fuels have superior combustion characteristics, which result in a more uniform turbine performance. Because they are cleaner, fuels can more easily meet the stringent gas-quality requirements of gas turbines and produce even fewer emissions than bulk biomass. Finally, fuels can be produced from a large number of biomass resources, including agricultural residues, crops dedicated to producing energy, and municipal waste.

Pyrolysis technologies

NREL has been developing the ablative pyrolysis concept since the early 1980s, and the process has been tested at the 20–35-kg/h scale (Diebold & Stevens, 1989). Biocrudes produced at 500°C and a 1-s residence time and containing water have about the same oxygen and energy content as the original feed, are fluid, and have a density of 1250 kg/m³. The process is

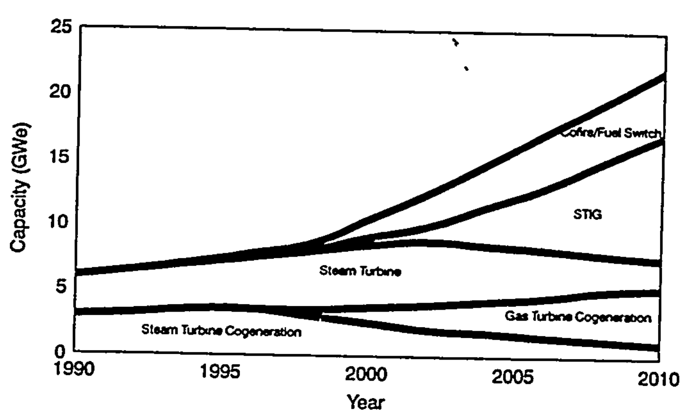

Fig. 3. Biomass-power market projections: installed capacity.

being scaled to 32 tonne per day by Interchem Inc., of Kansas City, Kansas, USA. The reported capital cost of this plant is about $750 000. Georgia Tech Research is developing an entrained-flow fast pyrolysis in which powdered wood is pyrolyzed in a tubular reactor using hot combustion-flue gases to provide reaction heat. Feed rates are about 15 kg/h, and the reported yields are about 58% organic condensates and 12% char. The University of Waterloo in Canada is developing a fluid-bed fast-pyrolysis process, and a 100 kg/h unit is in operation. The process has been scaled to 500 kg/h by the Union Electrica Fenosa in the province of Galicia in north-west Spain. It is understood that construction of this plant is complete and that the plant is in operation. ENSYN Technologies, Inc., Canada, is marketing a two-stage, sand-heated pyrolysis-reactor system. The first stage is a turbulent biomass/hot sand mixing zone, followed by a second-stage pyrolysis-reaction zone. Plants operating at 100 kg/h and 25 tonne/day have been constructed and are operating at Red Arrow in Wisconsin to produce smoke flavorings. Many of these systems were discussed at the International Energy Agency's Interlaken Conference (Coattam, 1992).

Gasifier technology

A number of gasifiers have been developed in the USA and Europe to produce low- and medium-heating-value gases from biomass and peat. In Europe, gasifier systems include fixed-bed gasifiers, such as the Bioneer gasifier (Kurkela, 1989), high-pressure gasifiers, such as the High Temperature Winkler (Koljonen, 1990), which has been demonstrated at the 600-tonne per day scale at the Kemira Chemical Company in Finland, and circulating-fluid-bed gasifiers, such as the Studsvik (Dhargalkar, 1991), Götaverken (Olauson, 1991), Ahlstrom (Lyytinen, 1987), and Lurgi (Loeffler, 1991) gasifiers. In the USA, gasifiers are being developed by the Institute of Gas Technology (Evans, 1988), the Battelle Columbus Laboratory (Feldmann, 1988), the University of Missouri at Rolla (Flanigan, 1988), and Manufacturing Technology and Conversion International (Scheifelbein, 1990). The IGT system is an air/oxygen fluid-bed gasifier. The other systems are indirectly heated gasifiers, using either entrained-flow or fluid-bed reactors. In a program funded by the Environmental Protection Agency, USDOE, and the United States Agency for International Development, a modified Lurgi-type fixed-bed gasifier using wood chips has operated to determine suitability for generating turbine producer gas. In addition, a number of commercial-scale gasifiers have been operated in the USA to produce low-Btu gas for use as plant fuel. Developers include Energy Products of Idaho, Halycon Industries, Morbark Industries, Producers Rise Mill, SEI, and Sur-Lite Corporation.

USDOE PROGRAM

NREL is the field manager for the USDOE biomass Power Program. The program is divided into two areas: R&D and systems analysis. The objectives of the R&D program are to develop advanced technologies for biomass conversion to electricity and to assist the existing industry in solving technical problems. The objectives of the systems-analysis program are to perform technical and economic analyses to support programmatic strategic analyses, to support the completion of site-specific feasibility studies for proposed conversion technologies, and to support demonstrations of novel technologies on a cost-shared basis.

In the R&D area, projects include the following.

- *Development of hot-gas cleanup systems to link gasifiers and turbines, with special emphasis on the impact of alkali-metal transport in gasification and combustion systems.* USDOE is currently negotiating a subcontract for the evaluation of high-temperature filters in conjunction with the operation of a pilot-scale, 10-tonne-per-day gasifier. In addition, research is being performed at NREL to develop an alkali-vapor-measurement system for laboratory studies of gasification and combustion, and an on-line organics-measurement system for field use.
- *Evaluation of alkaline deposits found in biomass-power plants.* The objective of this project is to organize and implement a joint NREL and industry investigation of possible solutions to the alkaline deposits experienced by the power industry. Results of the project are expected to benefit the existing industry, aid in the planning and design of new biomass-power systems, and identify needs for applied R&D. Fuels and deposits from existing biomass-power plants will be sampled and analyzed by using advanced techniques that have been used successfully to predict deposits in coal combustion. Selected fuels will be fired in the Sandia Livermore multifuel combustor, simulating actual furnace conditions. Deposits will be analyzed as they form and compared with deposits from the power plants. Industrial biomass experience will be catalogued in a plant-experience and fuels database that will eventually be made available to researchers and operating-plant personnel.
- *Biomass-pyrolysis research.* Research is being performed at NREL to generate biocrude by using ablative pyrolysis, to perform biocrude characterization and stability tests, and to develop techniques for alkaline-content minimization. In addition, a subcontract has been awarded to Sandia National Laboratories in Livermore, California, USA, to look at the combustion characteristics of biocrudes and pyrolysis chars. A series of laminar-flow-combustor experiments is being performed by using pyrolysis char in which the temperature is measured as a function of the particle diameter. The data from these experiments will be used to calculate burning rates and to develop kinetic expressions for combustion. Similar studies will be performed on single droplets of biocrude, by using a laminar-flow combustor currently under development.

In the systems-analysis areas, projects include the following.

- *USDOE gasifier scale-up.* USDOE and the State of Hawaii have joined with the Pacific International Center for High Technology Research (PICHTR) in a co-operative project to scale up the pilot-development-unit (PDU)-scale Institute of Gas Technology (IGT) RENUGAS pressurized air/oxygen gasifier to a 45–90-tonne/day Engineering Development Unit (EDU) operating at 1–2 MPa and using bagasse and wood as feed. Other participants in the project are IGT, the Hawaii Natural Energy Institute (HNEI), the Hawaii Commercial and Sugar Company (HC&S), and the Ralph M. Parsons Company, the architectural and engineering (A&E) firm for the project. The project is located at the HC&S sugar mill at Paia, Maui, Hawaii, USA.

  The scale-up project will be completed in several stages. The first phase, which is now under way, consists of the design, construction, and preliminary operation of the gasifier to generate hot, unprocessed gas. The gasifier is being designed for operation with either air or oxygen at pressures of up to 2·2 MPa, at typical operating temperatures of 850–900°C. In Phase 1, the gasifier will be operated for about four months at a feed rate of 45 tonne/day at a maximum pressure of 1 MPa. After the end of Phase 1 in mid-1994, a hot-gas cleanup unit and gas turbine will be added to the system for the generation of 3–5 MW of electricity. In this phase, the gasifier feed rate will be 90 tonne/day, and the system will operate at pressures of up to 2·2 MPa. In Phase 3, the system will be operated in an oxygen-blown mode to produce a clean syngas for methanol synthesis in addition to producing electricity. The project is in the final stages of environmental permitting and detailed design for Phase 1.
- *Direct-fired turbine.* Power Generating Inc. (PGI), Fort Worth, Texas, USA, has developed and patented a direct-fired gas-turbine power system that is able to operate on solid fuels such as wood and coal. The PGI system is designed to generate from about 500 kW to 3·5 MW of electrical power for a variety of industrial and utility applications. The exhaust from the system can be used directly as a source of thermal energy or fed into a heat-recovery steam generator to produce steam. Full use of both types of energy allows the PGI system to operate at projected thermal-efficiency rates in excess of 70%.

  The project involves the design, construction, and operation of a 400-kW prototype demonstration system at the Western Research Institute (WRI) in Laramie, Wyoming, USA. The demonstration projects cost approximately $5.1 million and will last approximately 33 months. The project is jointly funded by the USDOE Office of Conservation and Renewable Energy, the USDOE Office of Fossil Energy, and PGI. The system will be operated by using clean wood and then coal. The results expected from the project are confirmation of the technical and economic feasibility of operating the direct-fired turbine-powered system on wood and coal and will provide a basis for the testing of additional fuels. The project is in the detailed-design phase.
- *Process analysis.* NREL is performing technical and economic analysis of developing technologies for biomass conversion to electricity. These studies include analysis of gasification and pyrolysis technologies by using a process simulator, ASPEN/SP, for material and energy balances, standard cost-estimating techniques for capital and operating costs, and discounted cash flow and levelized costs for process economics. For example, the production of biocrude has been recently studied (Gregoire, 1992) to determine the technical and economic characteristics of the process.

  A detailed process model was developed for the production of biocrude from wood chips. The process consists of four parallel process trains, each containing a silo dryer for the removal of water from the feed wood, a vortex reactor for the pyrolysis of the wood, a furnace to provide the required sensible heat and heat of reaction for the pyrolysis reaction, and a steam turbine to convert excess thermal energy into electric power. The pyrolysis vapors from the four trains are combined and enter a single recovery train. The produced biocrude is condensed and stored for shipping.

  Results of the simulation were used to size and cost major equipment items. Economic evaluation of the process was conducted to develop an understanding of the important parameters and to identify missing or incomplete data.

  A number of case studies were conducted to illustrate the importance of economic parameters on the perceived viability of the process. The analysis for a 907-dry-tonne-per-day (dtPD) facility indicated that, for $44/dry tonne wood chips and a 20% capital-recovery factor, the required selling price for the biocrude is 10¢/kg. A more accepted economic-evaluation technique is the determination of the discounted-cash-flow rate of return (DCFROR). For the nominal 900-dtPD facility, the required selling price for the biocrude in order to receive a 25% rate of return was 14·7¢/kg. This is equivalent to petroleum, on a contained-energy basis, at 27·7¢/liter. If 50% of the required capital is borrowed, the required selling price is reduced to 10·1¢/kg or 19·5¢/liter.
- *Feasibility studies.* USDOE is committed to the performance of site-specific feasibility case studies on a cost-shared basis, with the objective of determining the technical and economic feasibility of new biomass-to-electricity technologies. USDOE has recently entered into a cost-shared project with the Tennessee Valley Authority (TVA) and the Electric Power Research Institute to evaluate the feasibility

being scaled to 32 tonne per day by Interchem Inc. of ... R&D and systems analysis. The objectives of the

of cofiring wood with coal in a number of existing TVA coal-fired stations.

LEGISLATIVE INCENTIVES

In November 1992, the Energy Policy Act of 1992 (EPACT) became law in the USA. Included in EPACT are a number of provisions (House of Representatives, 1992) that impact the development of biomass power.

In Title XII, Section 1201, 'Demonstration and Commercial Application Projects', the USDOE is authorized to solicit cost-shared demonstration projects for renewable energy. A maximum authorization of $50 million is permitted, and the initial solicitation of proposals should take place in 1993.

In Title XIX, Section 1914, provision is made for a 1·5c/kWh tax credit for electricity produced from closed-loop biomass, in which closed-loop biomass is defined as biomass that is planted, grown, and harvested on a dedicated basis for electricity production.

SUMMARY

In this paper, a discussion of the status of the USA, power industry has been presented, describing the potential for growth of the industry from its present size of 6 GW to 20 GW in 2010, and potentially to more than 100 GW by 2030. The rationale for this development was discussed, including environmental and economic impacts. Finally, a brief description of the ongoing USDOE program to assist the development of the biomass-to-electricity process was given.

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OVERVIEW OF THERMOCHEMICAL BIOMASS CONVERSION

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ABSTRACT

Thermochemical conversion technologies offer the potential of converting biomass feedstocks into liquids and chars for use either as fuels or as chemical feedstocks to replace the current dependence on fossil fuels. There have been considerable research, development, demonstration and commercialization activities underway in Canada over the past years in the promotion of pyrolysis and gasification technologies. This paper will highlight the technical developments and current status of these various thermochemical systems and describe future R & D directions. In the pyrolysis area, a major focus of the Canadian government is the generation of power from these bio oils through steam cycle systems, diesel engines or gas turbines and the current status of these projects will be discussed. Additionally, some work is underway on the production of value added chemicals from the pyrolysis oils and this will be discussed. An R & D project on the gasification of processed municipal solid waste will also be discussed.

OVERVIEW OF CANADIAN THERMOCHEMICAL BIOMASS CONVERSION ACTIVITIES

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OBJECTIVE

PROMOTE THE RESEARCH, DEVELOPMENT AND COMMERCIALIZATION OF TECHNOLOGIES UTILIZING BIOMASS AND WASTES AS A SUBSTITUTUE FOR NON-RENEWABLE FOSSIL FUELS AND PETROCHEMICAL FEEDSTOCKS.

IN SUPPORT OF GOVERNMENT POLICIES PROMOTING ENERGY DIVERSITY FOR CANADA'S FUTURE IN AN ENVIRONMENTALLY SUSTAINABLE CONTEXT.

	$'000 (CDN)
1. BIOFUEL HANDLING	700
2. COMBUSTION	900
3. BIOCHEMICAL CONVERSION	1,300
4. THERMOCHEMICAL CONVERSION	1,000
TOTAL	3,900

GREENPLAN

ETHANOL FROM WASTE	350

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INDUSTRIAL ENERGY CONTRIBUTION

- 367 PJ (17%) OF INDUSTRIAL ENERGY DEMAND (>OIL OR COAL)
  - 100 PJ FROM SOLID WOOD RESIDUE
  - 267 PJ FROM SPENT SULPHATE LIQUOR
- 1040 MW OF ELECTRICAL GENERATION (WOOD WASTE)
- 100 MW OF ELECTRICAL GENERATION (LANDFILL GAS)
- 20 PJ FROM MSW

RESIDENTIAL ENERGY CONTRIBUTION

- 170 PJ (14%) OF RESIDENTIAL ENERGY DEMAND
- 1.4 M DWELLINGS USE WOOD HEAT ENTIRELY OR SUPPLEMENTALLY

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(Abundant Resource Supply)

- Waste Feedstocks available at low or negative costs

		(Million tons per year)
Industrial Waste (wood):	Production	18
	Utilization	10
	Surplus	8
Municipal Solid Waste:	Production	30
	Use	1
Demolition Wood:	Production	14
	Use	3
Forest Waste:	Production	29
	Available	16
Crop Residues:	Available	43
Sludges:	Primary	1.4
	Secondary	0.25
	Deinking	0.32

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Industrial Wastes:	-	Quantities Declining
	-	More Remote
	-	Lower Quality
Forest Wastes:	-	Dispersed
	-	Quantities Increasing
	-	Environmental Sensitivities
Municipal Wastes:	-	?
Demolition Wastes	-	Quantity Increasing
	-	Environmental Sensitivities

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[redacted]

- ENERGY DEMAND OPPORTUNITIES
  - MUNICIPAL SOLID WASTE — 40 PJ
  - INDUSTRIAL WASTE — 15 PJ
  - REPLACEMENT IN FOREST INDUSTRY OF PURCHASED FOSSIL FUEL WITH BIOMASS — 150 PJ

- INCREASING ENVIRONMENTAL PUSH
  - CO_2 REDUCTION
  - WASTE UTILIZATION
  - LOW SULPHUR

- INCREASED ACCEPTANCE ON THE PART OF UTILITIES AND INDUSTRY OF THE POTENTIAL OF WOOD BASED ELECTRICITY GENERATION

- INCREASING ECONOMIC VIABILITY FROM EMERGING CHEMICAL PRODUCTION FROM OILS

- RENEWABLE ENERGY TECHNOLOGIES BECOMING COST EFFECTIVE IN NICHE MARKETS

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- LOW AND STABLE ENERGY PRICES
- LACK OF ENVIRONMENTAL REGULATIONS
- ENERGY SECURITY NO LONGER AN ISSUE
- LACK OF COMMERCIAL AND DEMONSTRATION UNITS
- BIOENERGY INDUSTRIES STILL SMALL WITH LIMITED CAPITAL RESOURCES AND INFRASTRUCTURE
- REQUIREMENTS TO ESTABLISH "DEVELOPMENT" INDUSTRY TO INTRODUCE THE TECHNOLOGY TO ESTABLISHED INDUSTRY

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OBJECTIVE

TO DEVELOP AND COMMERCIALIZE COST COMPETITIVE PROCESSES TO PRODUCE LIQUID AND GASEOUS FUELS AND CHEMICALS FOR:

- PROCESS HEAT
- ELECTRICITY GENERATION
- REFINERY FEEDSTOCKS
- TRANSPORTATION FUELS

ACTIVITIES - PYROLYSIS

- DEMONSTRATION/SCALE UP
  - UNIVERSITY OF WATERLOO - WATERLOO FAST PYROLYSIS PROCESS
    - 200 KG/HR UNIT BASED ON FOREST WASTES (IN COOPERATION WITH UNION FENOSA)
  - WORTHING INDUSTRIES
    - 400 KG/HR MOBILE UNIT TO TREAT USED UTILITY POLES
  - UNIVERSITY OF LAVAL - VACUUM PYROLYSIS
    - 200 KG/HR SYSTEM FOR USED TIRES AND AUTOMOBILE SHREDDER RESIDUE
  - CASTLE CAPITAL - CONTINUOUS ABLATIVE REGENERATOR
    - 1500 KG/HR UNIT FOR TIRES, BIOMASS AND MSW

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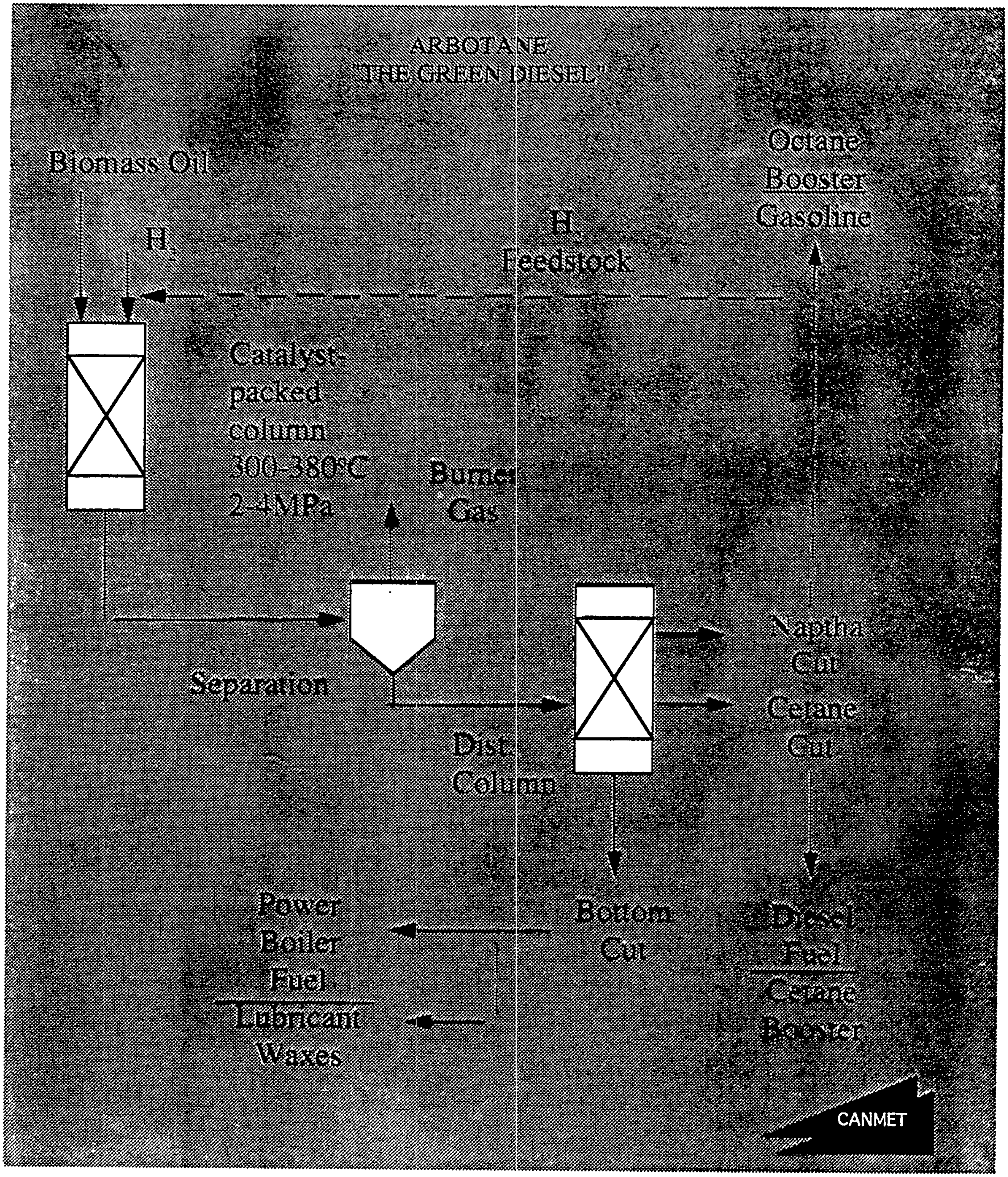
ARBOTANE
"THE GREEN DIESEL"
Biomass Oil
H₂
H₂
Feedstock
Octane
Booster
Gasoline
Catalyst-
packed
column
300-380°C
2-4MPa
Burner
Gas
Separation
Naptha
Cut
Cetane
Cut
Dist.
Column
Bottom
Cut
Power
Boiler
Fuel
Lubricant
Waxes
Diesel
Fuel
Cetane
Booster
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- DEMONSTRATION/SCALE UP (CONT'D)
  - ENSYN TECHNOLOGIES - RAPID THERMAL PROCESSING
    - 2000 KG/HR UNIT RUNNING IN USA
    - ADDITIONAL UNITS PLANNED FOR CHEMICALS, FUELS AND POWER GENERATION APPLICATIONS

- FUEL CHARACTERIZATION , OPTIMIZATION AND UTILIZATION
  - CHARACTERIZATION, UPGRADING AND STABILIZATION STUDIES
  - COMBUSTION SYSTEMS
  - GAS TURBINES
  - DIESEL ENGINES
  - CO-FIRING

- VALUE ADDED CHEMICALS
  - SEPARATION AND REFINING TECHNOLOGIES FOR PYROLYSIS OIL
  - FURTHER INVESTIGATIONS OF APPLICATIONS FOR PYROLYSIS OIL FRACTIONS

EMR - AgCan Hydroprocessing Project

Fuel Properties of Super Cetane

Density	0.87 kg/m^3	Carbon Res.	0.05 % wt.
Cloud	24 °C	Ash	<0.002 % wt.
Pour	21 °C	Kinematic Viscosity	3.74 cSt
Sulphur	0.002 % wt.	Copper Strip	Nil
Flash	138 °C	Cetane No.	90 $^+$

- CONTINUED COMMERCIAL SCALE UP OF PYROLYSIS TECHNOLOGIES
- ADDITIONAL TESTING OF BIOMASS WASTES HAVING DISPOSAL PROBLEMS
- UPGRADING, CHARACTERIZATION AND STANDARDIZATION OF PYROLYSIS OILS AS A FUEL REPLACEMENT
- TESTING OF PYROLYSIS OIL AS A FUEL IN BOILERS, DIESEL ENGINES AND GAS TURBINES
- DEVELOPMENT OF NEW MARKET APPLICATIONS FOR PYROLYSIS FRACTIONS
- DEVELOPMENT AND DEMONSTRATION OF PRODUCT FRACTIONATION AND RECOVERY PROCESSES

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CELLULOSE PYROLYSIS KINETICS: THE CURRENT STATE OF KNOWLEDGE†

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Abstract

Recent advances in experimental methods and computer modeling have shed new light on the kinetics of cellulose pyrolysis. The rich slate of reaction products that evolve when cellulose is heated implies that the pyrolysis chemistry is exceedingly complex. Nevertheless, a simple, first order, high activation energy (ca. 238 kJ/mol) model accurately describes the pyrolytic decomposition of an extraordinary variety of cellulosic substrates. Secondary vapor-solid interactions are the main source of char formed during cellulose pyrolysis. When a whole biomass substrate is pretreated to remove mineral matter, the pyrolysis kinetics of its cellulose component are very similar to those of pure cellulose. Future work should focus on the effects of mineral matter on pyrolysis, and the secondary, vapor-solid reactions which govern char formation.

† This review is dedicated to Dr. Patrick K. Takahashi, Director of the Hawaii Natural Energy Institute and Professor of Civil Engineering, University of Hawaii at Manoa.

Conclusions

1. Under conditions which minimize vapor-solid interactions and heat transfer intrusions, the TGA and DTG curves associated with the pyrolysis of a wide variety of pure cellulose samples can be well fit by an irreversible, single-step, first order rate equation with a high activation energy (ca. 238 kJ/mol).

2. DTG curves obtained from the pyrolysis of cellulose samples contaminated with a small amount of hemicellulose can be resolved into peaks derived from the decomposition of the substrate's two components. Likewise, DTG curves associated with the decomposition of pretreated (so as to remove mineral matter) samples of whole biomass can be resolved into peaks associated with the pyrolysis of the sample's cellulose and hemicellulose components, as well as a shifting baseline due to lignin decomposition. In both cases, the cellulose peak can be well fit by a high activation energy, first order, single step model.

3. This first order, high activation energy, single step model accurately mimics the weight loss behavior of cellulose over a wide range of heating rates, providing vapor-solid interactions and heat transfer intrusions are minimized.

4. Thermal pretreatments of a few hours do not reduce the ability of this model to fit cellulose TGA and DTG curves.

5. In light of items 1-4 above, we conclude that, under conditions of commercial interest, small samples of pure cellulose undergo thermal decomposition by a single, first order, high activation energy, rate determining step.

6. Prolonged (ca. 15 hours) thermal pretreatments at temperatures between 250 and 290 °C are needed to evoke the competitive reactions which underpin the models of Broido and Shafizadeh. When such pretreatments are applied, a simplified Broido-Shafizadeh model (which lacks an initiation step) can achieve a good fit to TGA data. Because commercial practice does not usually involve prolonged thermal pretreatments, the models of Broido and Shafizadeh are not relevant to the design of biomass combustors, gasifiers, and flash pyrolysis reactors.

7. Vapor-solid interactions (secondary reactions) are effectively the only source of char formed during the pyrolysis of a pure cellulose. These heterogeneous reactions alone can increase the cellulosic char yield from 0% to more than 40%. Some evidence suggests that the vapor-solid reactions are catalyzed by water vapor. These reactions are key to the efficient (high yield) manufacture of charcoal from biomass.

8. As indicated by the high activation energy model, the rate of cellulose pyrolysis is extremely sensitive to temperature. Also, the devolatilization reaction is strongly endothermic. A consequence of these two facts is that extraordinary heat demands exist when cellulose decomposes at high temperatures. Unmet heat demands (eg. heat transfer intrusions) are one explanation for the occasional kinetic study which reports a low activation energy (ca. 130 kJ/mol) for pure cellulose pyrolysis.

9. Minute amounts of mineral matter naturally present in whole biomass samples strongly catalyze the decomposition of the cellulose component in unpredictable ways. Pretreatments involving a hot water wash, or a dilute acid wash, can remove the offending mineral matter. Pretreated in this way, the cellulose component of biomass substrates enjoys pyrolysis kinetics which are effectively identical to those of pure cellulose samples.

10. Little is known concerning the kinetics of the mineral matter catalyzed pathways which enhance the formation of glycolaldehyde from cellulose.

11. In light of the obvious importance of the secondary, vapor-solid reactions which lead to char formation, more attention should be given to methodical studies of the influence of particle size on pyrolysis chemistry and kinetics. Similarly, methodical studies of the influence of mineral matter content on pyrolysis products and rates merit emphasis. The field is still far from its goal of being able to predict the pyrolysis behavior of whole biomass feedstocks (such as wood chips) in a chemical reactor.

Chemical Analysis of Biomass Fast Pyrolysis Oils.

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This paper reviews developments in the field of chemical analysis of biomass fast pyrolysis oils. The techniques applied to pyrolysis oil analysis are reviewed, including proximate and ultimate analysis, water (moisture) analysis, and chemical component analysis by various forms of chromatography, solvent separations, and infrared spectrophotometric analyses. Advanced analytical techniques such as nuclear magnetic resonance and molecular beam-mass spectrometry are also discussed. This paper reviews and compares the methods and the results of the analyses. The advantages and shortcomings of the various methods applied are also identified. Comparisons derived from the IEA Round Robin have been incorporated.

INTRODUCTION

Historically, biomass fast pyrolysis oil analysis can be traced back to the analysis of wood pyrolysis tars and condensates. Early attempts at analysis settled for some primary component quantitation, such as acetic acid, methanol, and "tars"[1]. However, the great complexity of the pyrolysis organic products was recognized from the earliest attempts at fractionation and analysis[2]. With the development of flash pyrolysis processes for biomass, analytical efforts began anew to determine the composition of the product oils. An initial effort was made as part of the International Energy Agency activity, Biomass Liquefaction Test Facility (IEA-BLTF). The final report from that activity[3] included a variety of data about fast pyrolysis products produced from wood and peat at several facilities in the U.S. and Canada. Analyses included elemental analysis, ash, moisture, heating value, density, viscosity, organic

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component identification by gas chromatography (GC) and mass spectrometry (MS), pour point, flash point, solvent insolubles, distillation curves, and infrared (IR) spectra. A second comprehensive effort at analyzing fast pyrolysis oils is presented in the final report of the Biomass Liquefaction: Centralized Analysis effort funded by the Energy, Mines and Resources Ministry of Canada[4]. Similar products were analyzed for ultimate composition, moisture, density, viscosity, organic component identification by both GC and liquid chromatography (LC) methods, simulated distillation and thermogravimetric analysis (TGA), molecular weight by osmotic pressure and gel permeation chromatography, nuclear magnetic resonance (NMR), and characterization by mass spectrometry-mass spectrometry and sequential elution solvent chromatography.

The results of these works, and other concurrent studies, convinced researchers of the difficulty of such a seemingly simple analysis as the carbon content of the oils. A round robin of oil analyses was organized through the IEA, within the Conversion Task of the Bioenergy Agreement, to compare results from various laboratories around the world doing research in the field. The elemental analytical results were highly dependent on the moisture determination in the product. The results showed significant variation, both intra- and inter-laboratory (see ref. 10).

CHEMICAL ANALYSIS TECHNIQUES

Ultimate Analysis -

Ultimate analysis (elemental analysis of carbon, hydrogen, nitrogen, and oxygen - sulfur being a trace component in the case of biomass oils) is a prerequisite for the elemental balance needed for sufficient engineering analysis of a biomass conversion process. This type of analysis has been available from the earliest papers describing fast pyrolysis[5,6]. For the most part, this analysis has been accomplished over the years by automatic instrumental methods using micro-sampling techniques. Sample size has been suggested as a factor in obtaining inconsistent results. The inhomogeneous nature of biomass fast pyrolysis oils could result in sampling variations due to the solid char and moisture content of the oils. The high moisture

content of the pyrolysis oil is generally considered to be dissolved in the oil; however, high moisture contents in the oils can lead to phase separation of a mostly water phase and a mostly organic phase (known in early pyrolysis literature as "settled tar," and more recently referred to as "pyrolytic lignin").

Moisture Analysis

When analyzing petroleum oils, the standard method for water determination is by codistillation with xylene in a Dean-Stark apparatus for samples with higher levels of moisture[7]. Karl Fischer titration is used to determine trace amounts of water[8]. For the biomass fast pyrolysis oils, the large amount of volatile organic components are found to be water soluble, leading to a falsely high determination for either codistillation or direct distillation of water[9]. Minor interference in the Karl Fischer titration has also been studied, but it was still considered to be the method of choice. Evaluation of GC for analysis of water in fast pyrolysis oils has also been reported[10].

Chemical Component Analysis

Instability of the products has inhibited complete analysis, particularly for GC analysis, which requires vaporization of the material. The high molecular weight components containing oxygenated, polar functional groups were at once the largest fraction, thermally unstable, and low volatility. Because of its wide availability, GC has been used extensively with the fast pyrolysis oils. Large tables of components have been identified (see ref. 3 and 4). The technique has been useful for directly analyzing both whole oil and fractionated oil[11]. Typically, MS is coupled to the GC for qualitative analysis, and quantitative analysis is accomplished with an internally standardized flame ionization detector. Unfortunately, much less than half of the oil is typically analyzed by GC.

LC has been used in several formats for analyzing the more polar components. Initial work[12,13] was later expanded to include methods to identify a suite of carbohydrates and a suite of carboxylic acids (see ref. 4).

Gel permeation chromatography (GPC) or size exclusion chromatography has also been used for molecular weight range measurement for the fast pyrolysis oils[14]. The whole is analyzed by this method. High molecular weight fractions were identified in the oils, but calibration of the technique is uncertain.

Solvent systems have also been used to separate components and facilitate analysis. Initial tests were simple solvent solubility/insolubility tests (see ref. 3). By these tests, it was concluded that the pyrolysis oils contained very little nonpolar material, but a measureable amount of insoluble char material. Later systems have incorporated standard acid/base fractionation with organic solvents to determine, in detail, the small amount of condensible hydrocarbons produced in biomass fast pyrolysis[15]. Another technique used was sequential elution solvent chromatography (see ref. 4). Although information was obtained on the relative polarity of the components of the oil, the researchers concluded that the real value of the procedure was in fractionating the oil to facilitate analysis of the separate portions.

Advanced Analytical Methods

A wide range of modern and developmental analytical tools have been used to analyze biomass fast pyrolysis oils. Infrared spectrophotometry, for example, was found to be of limited use for analyzing the whole oil products (see ref. 3), but helped to further define some oil fractions when used in combination with other instrumental methods[16](see also ref. 11).

Nuclear magnetic resonance has been used extensively, and both proton and carbon-13 spectra have been obtained. The technique has been appplied to both whole oils[17] (see also ref. 4 and 12) and oil fractions (see ref. 11). Carbon-13 analysis was concluded to be more useful in defining the biomass fast pyrolysis oils because of the lack of water interference and less sensitivity to paramagnetic materials in the oils[18]. Little difference can be seen among the various fast pyrolysis oils tested to date.

The use of molecular beam-mass spectrometry (MB-MS) at the National Renewable

Energy Laboratory has been reported widely[19]. Much data have been reported, and comparisons among the various oils made. A similar technique is the MS-MS, which has been investigated to a limited degree (see ref. 4). Further development is required, especially for higher molecular weight components. Pyrolysis mass spectrometry has also been reported (see ref. 4).

Thermal Fractionation

Thermal means have also been used to fractionate biomass fast pyrolysis oils. Analogous to petroleum oil analysis distillation, both vacuum and atmospheric pressure distillations have been reported (see ref. 3). Thermal instability of the oil limits the amount that can be recovered as volatile product by these methods. Simulated distillation is routinely performed on a GC with petroleum oils. Similar tests with pyrolysis oils give results with only limited correlation to actual distillation (for results see ref. 4). TGA can also provide information similar to a distillation; however, it can not distinguish between actual distillation and thermal decomposition to volatile products (for results see ref. 4). Residual carbon analysis can also be simulated with TGA methods.

CONCLUSIONS

The amount of data from chemical analysis of biomass fast pyrolysis oils has grown substantially in the past 10 years of the process development era. Few differences exist in the products from the various reactor systems being engineered. The differences in oil composition because of variations in the feedstock have been more definitively determined. The oils are a complex mixture of oxygenates and water. Specific identification and quantitation of the individual components is a challenge, even for the modern chemical analysis laboratory.

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THE ULTIMATE ANALYSIS OF BIOMASS LIQUEFACTION PRODUCTS: THE RESULTS OF THE IEA ROUND ROBIN #1

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ABSTRACT

The first IEA thermochemical round robin was organized as part of an IEA Voluntary Standards Activity. The objective of the study was to determine the variability associated with the measurement of carbon, hydrogen, oxygen and water in biomass oils using those techniques normally employed at each laboratory. Two biomass oil samples were distributed to fifteen laboratories in November, 1988. One sample was a low oxygen content condensed oil (PERC oil ex Albany) and the second was a high oxygen and water content primary oil (WFPP oil ex University of Waterloo).

The precision for carbon was excellent, whereas, both the hydrogen and oxygen (by difference) values were more variable. Oxygen (by direct determination) was poor. The water content was quite variable and it had a strong influence on the carbon and hydrogen estimates (on a dry basis) which in turn had a significant effect on the H/C ratio of the biomass oil. The coefficients of variation for the H/C ratios of the two oils are very markedly different in that the PERC oil has a value of 5%, which is in the range anticipated, while that of the WFPP oil was 19.5%. The study is the first examination on this topic and the information derived from it will be used to critically assess laboratory procedures and evaluate the comparison of inter-laboratory data. It is recommended that future studies of this nature include a wider variety of samples so that trends are easier to establish.

KEYWORDS: LIQUEFACTION OIL ULTIMATE ANALYSIS IEA VOLUNTARY STANDARDS ROUND ROBIN

INTRODUCTION

The use of biomass for energy in forms that are compatible with the demands of modern industrial societies requires that the raw biomass be converted into refined products having well specified properties that are suitable either for direct end use, or for further upgrading. One of the techniques of current interest is

the direct conversion of lignocellulosic biomass into an oil. These oils can be produced by direct pyrolysis or in hydrogenation reactors of various kinds. In order to compare and contrast their properties with the traditional fuels, these oils must be subjected to chemical and physical analyses.

The commercialization of refined biomass fuels and processes will depend in part on the confidence that can be expressed in these analyses. The International Energy Agency's Biomass Program in Denver in 1987 agreed to a voluntary standards activity comprising the development of biofuels related reference materials and the evaluation of some of the tests in current use in a series of round robins[1].

The thermochemical panel at the Denver meeting identified the ultimate analysis of biomass feedstocks and products as one of the basic measurements necessary to describe and evaluate process concepts and efficiencies since for each process stream the carbon, hydrogen, oxygen and nitrogen (abbreviated hereafter as CHON) balance is required. There was almost unanimous agreement in the panel that there was considerable confidence in the reliability of the C, H, O, N, and S measurements. These methods, however, were developed primarily for more traditional hydrocarbon fuels and while the adaptation to bio-materials was commonly held to be successful, it was also recognized that this had not really been critically evaluated. Thus the measurement of CHON and moisture content of two very different biomass oils was proposed as the first round robin. The oils were derived from two processes in North America; the PERC process at Albany[2], and the WFPP or Waterloo Fast Pyrolysis Process[3].

The oils had already been characterized in some detail in the R&D programs associated with the PERC process[4] and for the WFPP by Piskorz et al.[5]. They are both very heterogenous in composition and while the former oil is low in oxygen and moisture, the latter is very oxygenated and contains a lot of associated water.

Following several discussions among potential participants, a total of 15 laboratories agreed to participate in one or more of the measurements proposed. These laboratories, and the researchers who led the laboratory efforts, are detailed in Appendix 1. These laboratories are identified in this report by two digit numerical codes that were assigned randomly to the participants.

The Canadian Biomass Development Program agreed to finance the preparation of samples and their distribution through the laboratories of British Columbia Research (BCR) who prepared the well-mixed lots of the oils and packaged them during the fall of 1988. The samples were sent out to the participants the week of October 9, 1988.

MATERIALS AND METHODS

The Liquefaction Oils

The Waterloo oil produced in the Waterloo Fast Pyrolysis Process, was from the treatment of hardwood, Poplar at 500°C for 500 ms. The PERC oil was a TR-12 oil from barrel 807 (labelled "Composite TR-12 Oil"), and was produced at the Albany, Oregon, facility in 1981 from Douglas Fir slurried in a wood based recycle oil and treated for 35 s in the heater (outlet temperature of 370°C), and then at 330°C for 18 min in the reactor, the pressure was 3,000 psi, with a Na_2CO_3 catalyst.

The Research Strategy

The round robin involved the 15 laboratories in the analysis for CHON and moisture on the two oil samples. The determination of oxygen by difference would be perturbed by the ash content, so this was assayed separately by BCR. Since the round robin estimates the inter-laboratory differences, it was decided that one laboratory should be utilized to establish an estimate of the intra-laboratory precisions on the measurements. This laboratory was a commercial laboratory, that over a period of two months received several batches of pyrolysis oils from the Canadian liquefaction program. Included in each of the sample batches was the WFPP oil. The results labelled intra-laboratory are therefore a longitudinal series, all performed by the same laboratory. All participating laboratories were requested to follow their normal procedures, irrespective of whether or not they did the analyses in-house or extramurally. The results were to be reported as they normally would be.

Our analysis of the results is conducted on the following basis. We do not know the **correct** CHON values for the two oils. The question we are trying to answer is whether the standard elemental and water analyses are satisfactory in terms of their final application, i.e. would two laboratories using the same process and feedstock report the same oil quality? For this we have assumed that the quality criteria that would be used by most laboratories would be the H/C and O/C ratios (measured on a dry basis), since these determine the extent of upgrading towards a hydrocarbon-like product. Thus our final comparison of all of the laboratories is in terms of these ratios which we would assume to be the final reported significant result.

In order to determine the most likely value of these ratios, we have examined the raw data for outliers and then determined the mean and standard deviation of each of the elements and then by means of statistical error propagation generated the **most probable values or MPV** of the mean and standard deviation of each of the ratio determinations. We have therefore assumed that the individual element and the water determinations are not correlated.

Analysis Methods Used by Participants

All of the laboratories except two, reported on the instrumental analyzers and methods used, and these are tabulated in Table 1. The majority of the water determinations were by Karl Fischer titration; one laboratory reported a Dean and Stark determination and another furnished, in addition to the Karl Fischer determination, values obtained by a gas chromatographic method using two different solvents.

RESULTS

The data as received consists of the reported values of carbon, hydrogen, nitrogen, and oxygen by both difference and direct measurement along with the water determination. There are three data sets: an intra-laboratory determination of the values for the WFPP oil undertaken as blind samples by a commercial laboratory over a period of two months; the inter-laboratory determination by all of the laboratories for the WFPP oil, and the inter-laboratory determination of the parameters for the PERC oil sample. In all, 15 laboratories participated in the inter-laboratory comparison, though at the time of the data analysis, only 13 had reported C, H and O values and two had reported water results only. During the late stages of the preparation of the manuscript, one of these laboratories contributed the C, H, and O data in addition to additional water values determined by gas chromatography. These additional data were not used in the calculation of the **MPV's** for the oils, but were utilized in the final analysis of how well the laboratories compare. The laboratory results as received are all given in Table 2.

The Calculation Methodology

The data for each of the inter-laboratory determinations was plotted as box-plots that show the median value and the width of the quartiles of the data set. This was done on the basis of 13 of the laboratories that had reported at the time of the data analysis.

The box plot[6] is an extremely useful tool for visualising a data distribution. Figure 1 shows the essential features of a box plot. The centre line is the median value or 50th percentile of the data. The difference between the 75th percentile and the 25th percentile is defined as the inter-quartile range. Unusual values or outliers are considered to be those that are at least 1.5 times the interquartile range away from the appropriate quartile and are marked by an isolated point. If the value is within this range it is connected to the box-plot by means of a whisker.

Figure 2 shows the inter-laboratory data for the two oils and their elemental analysis as box-plots. In the case of the WFPP Oil carbon results, one value is a low lying outlier. The laboratory

not included in this stage of the analysis would also have furnished an outlier in the same location. The carbon determination for the PERC oil has a similar distribution to that of the Waterloo oil without an outlier. Both oils have an outlier in the water determination and it is evident that the water determination for the Waterloo oil has both a very large range and is not very symmetric. The hydrogen data also shows some significant difference between the two oils in terms of their spread along with one very low value of the hydrogen in the WFPP oil. Both oils contain very little nitrogen, though once again the Waterloo oil appears to have a greater spread of data than that of the PERC oil.

<u>Best Estimates or the MPV of the C, H, O and Water Values</u>

The mean and standard deviation of each of the element determinations were calculated for each oil along with those of the <u>intra</u>-laboratory determination on the WFPP oil. These values are presented in Tables 2 and 3.

The elemental carbon determination stands out in that it is the most precise, with standard errors of 1.43%, 1.18% and 0.98% for the WFPP-<u>intra</u>, WFPP-<u>inter</u> and PERC-<u>inter</u>, respectively.

The hydrogen determination is not so precise, the standard error on the WFPP-<u>intra</u> and the PERC-<u>inter</u> are similar at 1.15% and 2.12%, while that of the WFPP-<u>inter</u> is 6.62%. This lack of precision on the hydrogen will manifest itself later by the large standard deviation on the H/C ratio of the oil as calculated on a dry basis.

The precision of the nitrogen determinations is, as would be expected for the low nitrogen containing oils, rather poor. As can be seen in Figure 2, the distribution of the data points received in the <u>inter</u> laboratory determinations is non-symmetrical and the standard errors are 12%, 63% and 175% in the order WFPP-<u>intra</u>, WFPP-<u>inter</u> and PERC-<u>inter</u>, respectively.

The oxygen was determined by both the difference method and by direct determination. The former is the more usual method and in organizing the round robin it was hoped that it would be possible to make a comparison between the two methods. The standard error on the difference determination was 1.32%, 1.48% and 3.64% in the order used above. The first two for the WFPP oil are close to the values determined for the carbon as would be expected. The latter value for the PERC-<u>inter</u> determination is higher mainly because of the much lower content of oxygen in that oil. The direct method gave higher standard errors of 3.54%, 6.89% and 6.34%. Though the two <u>inter</u> laboratory determinations for the WFPP and the PERC oil have similar values for the standard error.

DISCUSSION

The WFPP Oil Intra- and Inter-Laboratory Comparisons

The inter- and the intra-laboratory results are very comparable both with respect to means and standard deviations for all elements with the exception of the direct oxygen determinations, in which the spread between the values of the participating laboratories is very large.

The most curious result concerns the difference between the values of the direct and indirect oxygen determination. The WFPP oil has almost no ash, the measured value being 0.022 percent by weight. Thus for the intra-laboratory data set, the oxygen by difference determination has a students 't' statistic of 5.42 which is significant at the p=0.001 level. The difference in oxygen means in the inter-laboratory set is not statistically significant while the standard deviations are, the 'F' statistic is as expected significant at the $p=10^{-3}$ level.

The PERC Oil Compared With the WFPP Oil Data

There was no intra-laboratory comparison made for the PERC oil. What can be seen by comparison with the Waterloo oil data is that the standard deviations in the measurements of carbon are similar and those for hydrogen are of the same order, though the PERC oil has less variation between laboratories. The water measurement is clearly superior for the PERC oil. There is a difference between the direct oxygen determination and the oxygen measurement by difference. An external determination of ash showed its value to be 3.38%. Adding this ash value to direct oxygen determination gives a predicted oxygen by difference value of 20.73 ± 1.10 at 1σ, while the actual difference value is 19.01 ± 0.76 at 1σ. While the "F" test shows us significance in the different variances, the difference in the means is significant at $p = 0.0015$.

LABORATORY ELEMENT RATIO DETERMINATIONS: COMPARED WITH THE BEST ESTIMATE

The H/C and O/C values for the two oils have been calculated using the oxygen by difference values only. The standard deviation of the best estimates are those calculated through the propagation of errors formula assuming that the measurements of each chemical element and of the water are uncorrellated.

The PERC Oil

The H/C atomic ratio calculated from the MPV element values was 1.236 ± 0.054 at 1σ. This statistical ratio is drawn as the solid line in Figure 3, which is a cumulative probability plot drawn on the appropriate transformation so that the line is linear. The

values calculated for each laboratory are then placed on the plot by making the assumption that they would be normally distributed around the mean. For seven of the reporting laboratories, this is seen to be a correct assumption. However, at the lower H/C ratios there are four laboratories that are deviating from the line and one at the highest value of H/C reported. This suggests that the overall distribution of laboratory results is "light" tailed relative to the Normal distribution.

The O/C ratio for the PERC oil is 0.155 ± 0.0082 at 1σ. Figure 4 is plotted on the same basis as that of Figure 3 and though the individual laboratory results are reasonably close to the line and can be considered to be close to a normal distribution, it would be possible to fit a line with almost the same mean value for the ratio, though with a greater standard deviation.

<u>The WFPP Oil</u>

The O/C ratio for the WFPP oil is 0.527 ± 0.047 at 1σ. Plotted on normal probability paper, Figure 5 the MPV line and the points are in good agreement with only one laboratory far from the normal distribution line.

The H/C ratio for the MPV is 1.353 ± 0.264 at 1σ. The standard deviation is far in excess of that calculated for the PERC oil, despite the standard deviations of the C and H measurements being similar. The large dispersion is entirely due to the influence of the hydrogen content of the water correction. In the WFPP sample, the hydrogen contained in the water is 33% of the total sample. The non-symmetric distribution of the water analyses is carried into the individual laboratory values and the fit with the MPV line is very poor. In fact, the laboratory data points can be considered to be on a line having a different mean value for H/C of 1.41 and standard deviation of 0.165. We interpret this difference to mean that the hydrogen and the water measurements are in fact correlated to some degree. Whereas the oxygen (indirect) and the water measurements are not.

OVERALL COMMENTS ON THE RESULTS

The results of the round robin are, on the whole, very reassuring. The dispersion of the individual laboratory results appear to be normally distributed and are thus due to random errors in all of the measurements with the exception of the measurements of water and hydrogen for the WFPP oil.

The evidence also suggests that indirect oxygen determination is satisfactory and that the direct determination is, on the whole, subject to greater imprecision. Though it is worrying that in 2 out of the 3 comparisons of the direct and indirect methods, the difference in values is in fact statistically significant.

Since the CHON measurement methods were developed primarily for hydrocarbon fuels and dry substances, it is no surprise that the low moisture content (4.4%) PERC oil with its H/C and O/C ratios of 1.24 and 0.054 respectively, behaved well in the round robin. It is also apparent that the TR-12 has less volatile constituents[4].

It is clear that the WFPP oil creates difficulties with the current CHON and water analyses. Roy and de Caumia[7] had already noted that some problems exist for the highly oxygenated pyrolysis oils in water determination. These problems could stem from the volatility of the light ends of the WFPP oil and the carbonyl oxygen content, a known problem with the Karl Fischer water estimation method. The magnitude of the problem with this oil can be seen by comparison of the coefficients of variation of the H/C and O/C measurements. For the PERC oil, they are 4.4% and 5.3% respectively; while, for the WFPP they are 19.5% and 9%.

CONCLUSIONS

The ultimate analysis of two pyrolysis oils by an international group of biomass research laboratories in a round robin has demonstrated that for the relatively condensed PERC TR-12 oil having low moisture content there is very good agreement between laboratories. The coefficients of variation of the H/C and O/C atomic ratios for the oil are both about 5% as determined between the laboratories. The distribution of the individual laboratory results appears to be "normal" (i.e. gaussian) around the mean values.

The results for the WFPP oil, a high oxygen and water containing oil, show that the precision of the carbon measurement is unchanged and that of hydrogen only slightly worse than that of the PERC oil. The measurements of oxygen and water are, however, of very low precision. This results in very low precisions for the atomic ratio determinations by comparison with the normal precision expected for these methods. It is likely that the oil is "difficult" on account of its volatility and chemical composition. In any case, the round robin has identified that further work is required in method development for these types of oils before the elemental ratios can be given to the same precision as normal samples.

Despite the time required to organize, analyze and collect the data from a large scale international round robin, the effort has proved to be very worthwhile in terms of scientific output and from the viewpoint of international collaboration. In new and emerging fields such as thermochemical biomass conversion technology, it is apparent that such collaboration should not only be encouraged but positively supported as this one was by the International Energy Agency.

ACKNOWLEDGEMENTS

The individual laboratories listed in Appendix 1 are thanked for their cooperation and donation of the results out of their normal programs. Financial support for the acquisition and distribution of the two oils utilized in this study was provided by the Bioenergy Development Program, Department of Energy, Mines and Resources Canada. A special recognition is given to Erin Skelton of the BC Research Corporation. She was responsible for the preparation and distribution of the samples, as well as for the collation of the results that were returned by the participating laboratories.

The authors dedicate this paper to the memory of R. Doug Hayes (1951-1989) who was one of the initiators and supporters of this IEA activity from the very beginning. His contribution to the development of both bioenergy and international collaboration was considerable and will be missed.

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Table 1. Summary of Methods

LAB NO.	CARBON, HYDROGEN, AND NITROGEN DETERMINATION	OXYGEN DETERMINATION	WATER DETERMINATION
14	PE 240C	N/D	KF MeOH
17	PE 240C	PE 240C	KF $CHCl_3$/MeOH
20	Leco 600	N/D	KF EtOH
21	PE 240	N/D	KF $CHCl_3$/MeOH
34	PE 2400	PE 240	KF MeOH
39	Carlo Erba 1104	N/D	KF $CHCl_3$
42	PE 240C	N/D	KF (Solvent N/A)
47	Carlo Erba 1108	N/D	N/D
49	PE (Model N/A)	PE (Model N/A)	KF (Solvent N/A)
51	N/A	N/A	N/D
57	N/D	N/D	KF (Solvent N/A)
66	Carlo Erba 1106	Carlo Erba 1106	KF $CHCl_3$/MeOH
69	N/D	N/D	KF MeOH GC MeOH GC THF
75	Leco 600	N/D	KF CH_2Cl_2/MeOH
86	Carlo Erba 1106	Carlo Erba 1106	Dean and Stark

N/D = Not Determined
N/A = Not Available
GC = Gas Chromatography
KF = Karl Fischer

Table 3: Results Summary

Waterloo Oil-inter-laboratory

Analysis	# points in set	Average	Standard Deviation
Carbon	12	43.19	0.51
Hydrogen	13	7.25	0.48
Nitrogen	13	0.34	0.21
Oxygen (Diff)		49.22	0.73
Oxygen (Dir)	5	47.43	3.27
Water	14	21.42	2.47

Waterloo Oil-intra-laboratory

Analysis	# points in set	Average	Standard Deviation
Carbon	10	43.91	0.63
Hydrogen	10	7.30	0.11
Nitrogen	10	0.20	0.022
Oxygen (Diff)		48.59	0.64
Oxygen (Dir)	10	44.03	1.56
Water	10	23.00	1.50

PERC Oil-inter-laboratory

Analysis	# points in set	Average	Standard Deviation
Carbon	14	72.64	0.71
Hydrogen	14	8.01	0.17
Nitrogen	13	0.12	0.21
Oxygen (Diff)		19.01	0.76
Oxygen (Dir)	5	17.35	1.10
Water	12	4.40	0.81

Note: Standard deviation for oxygen by difference is calculated by means of propagation of errors assuming that there is no covariance between the carbon, hydrogen and nitrogen values.

Table 2

IEA Test Results
Sample Waterloo

Lab	Carbon	Hydrogen	Nitrogen	Oxygen (Diff)	Oxygen (Dir)	Water	Atomic Ratios H/C	Atomic Ratios O/C
	On Sample As Received						Dry Basis	
69						24.10[a,b]		
69						21.10[a,b]		
69	39.93[a]	7.31			47.39	21.30	1.486	0.534
57						23.20		
47	42.70	6.22	0.07	51.01				
39	42.85	7.48	0.08	49.59		22.05	1.409	0.525
66	43.70	7.07	0.17	49.06	45.81	25.00	1.179	0.461
75	39.74[a]	7.64	0.19	52.43		23.42	1.522	0.597
51	42.60	6.35	0.20	50.85				
86	42.80	5.47[a]	0.24	51.55	51.45	30.13[a]	0.579	0.434
17	43.60	7.15	0.36	48.89	42.98	21.36	1.315	0.514
21	43.36	7.80	0.38	48.47		17.62	1.617	0.567
20	42.39	7.37	0.42	49.82		18.18	1.515	0.596
14	43.60	7.26	0.48	48.66		22.90	1.299	0.487
34	43.70	7.80	0.50	48.00	49.50	17.70	1.602	0.554
42	43.18	7.53	0.63	48.66		22.86	1.387	0.492
49	43.85	7.23	0.75	48.17	33.54[a]	18.83	1.407	0.538
Mean	43.19	7.25	0.34	49.22[d]	47.43	21.42	1.353[c]	0.527[c]
Std. dev	0.51	0.48	0.21	0.73[d]	3.27	2.47	0.264[c]	0.047[c]

[a]Not included in the estimate of the mean.
[b]Gas chromatographic values.
[c]Computed from the mean values for CHON, see text for discussion
[d]Calculation by propagation of error for 100-CHN.

Table 2 (Cont'd)

IEA Test Results
Sample PERC

Lab	Carbon	Hydrogen	Nitrogen	Oxygen (Diff)	Oxygen (Dir)	Water	Atomic Ratios H/C	Atomic Ratios O/C
	On Sample As Received						Dry Basis	
57						2.70		
69						4.57[a,b]		
69						3.98[a,b]		
69	72.83	7.92			17.34	4.37	1.225	0.139
47	72.90	8.00	0.00	19.10				
49	73.10	8.31	0.02	18.57	13.08[a]	4.13	1.289	0.153
42	73.31	8.36	0.04	18.29		3.65	1.302	0.154
39	73.13	7.94	0.09	18.84		4.97	1.212	0.148
17	73.60	7.99	0.11	18.30	16.93	4.44	1.222	0.146
66	72.80	7.91	0.12	19.17	17.12	6.13	1.191	0.141
21	73.14	8.00	0.12	18.74		4.88	1.224	0.148
86	72.60	7.99	0.14	19.27	19.17	4.26	1.243	0.160
51	71.50	7.88	0.16	20.46				
75	71.17	8.04	0.18	20.61		4.48	1.262	0.168
14	71.70	8.08	0.19	20.03		5.21	1.256	0.161
20	72.61	7.68	0.27	19.44		3.71	1.201	0.167
34	72.50	8.10	0.50[a]	18.90	16.20	2.10[a]	1.302	0.176
Mean	72.64	8.01	0.34	19.01[d]	7.25	4.40	1.236[c]	0.155[c]
Std. dev	0.71	0.17	0.21	0.76[d]	1.10	0.81	0.054[c]	0.0082[c]

[a]Not included in the estimate of the mean.
[b]Gas chromatographic values.
[c]Computed from the mean values for CHON, see text for discussion.
[d]Calculated by propagation of error for 100-CHN.

APPENDIX 1

Round-Robin Participants

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FIGURE CAPTIONS

Figure 1 Box Plot: Explanation of symbols

Figure 2 Distribution of the laboratory results for the PERC and WFPP oils shown as Box Plots for each element and water determination.

Figure 3 PERC oil O/C ratio plotted on normal probability distribution paper. Individual laboratory results shown as 69. The MPV (most probable value) distribution is given by the solid line.

Figure 4 PERC oil H/C ratio plotted on normal probability distribution paper. Individual laboratory results shown as 69. The MPV (most probable value) distribution is given by the solid line.

Figure 5 WFPP oil O/C ratio plotted on normal probability distribution paper. Individual laboratory results shown as 69. The MPV (most probable value) distribution is given by the solid line.

Figure 6 WFPP oil H/C ratio plotted on normal probability distribution paper. Individual laboratory results shown as 69. The MPV (most probable value) distribution is given by the solid line.

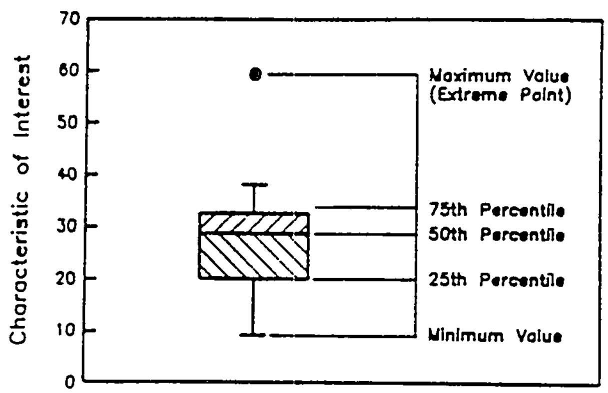
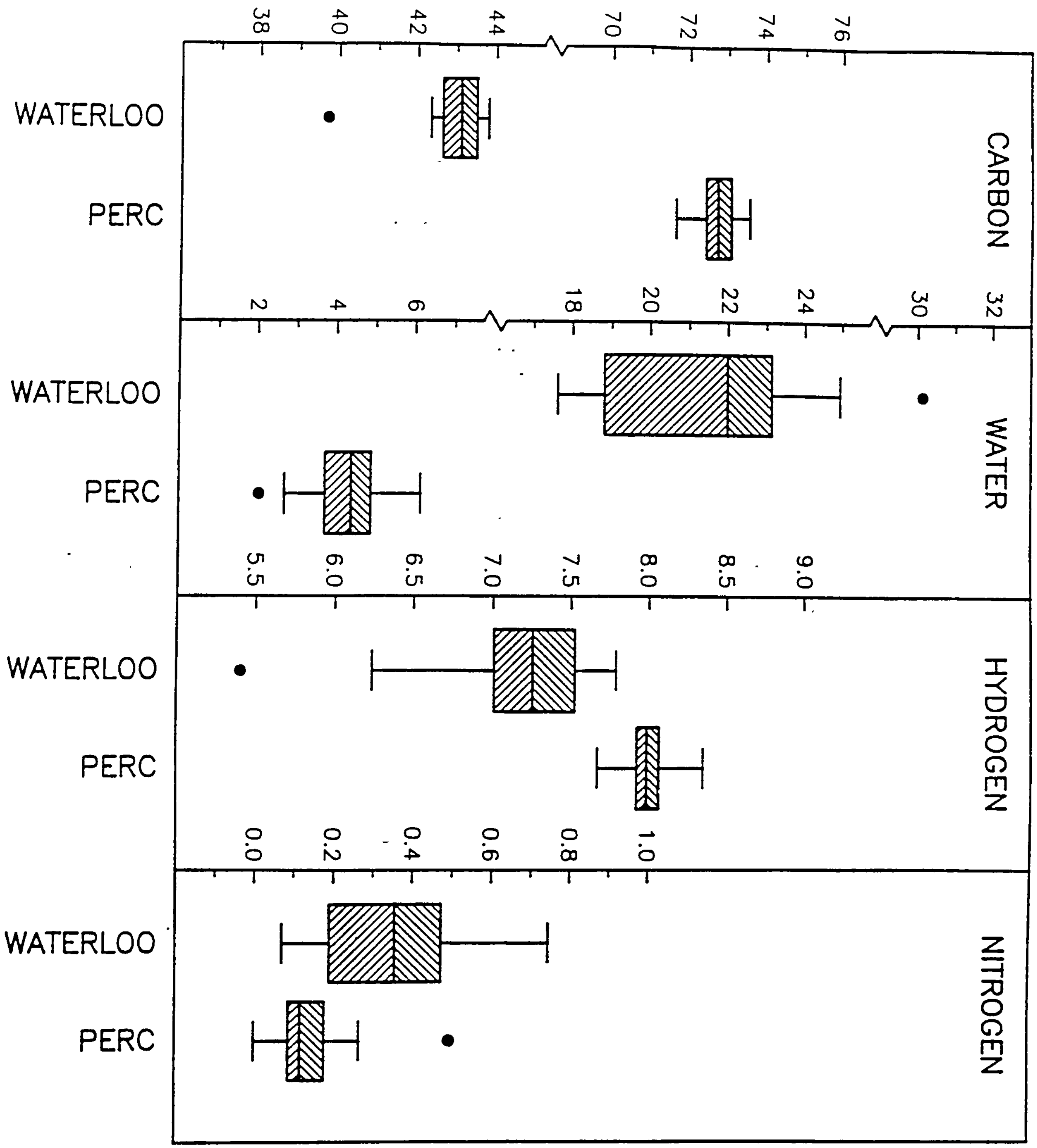


Figure 1 Box Plot: Explanation of symbols

Figure 2 Distribution of the laboratory results for the PERC and WFPP oils shown as Box Plots for each element and water determination.



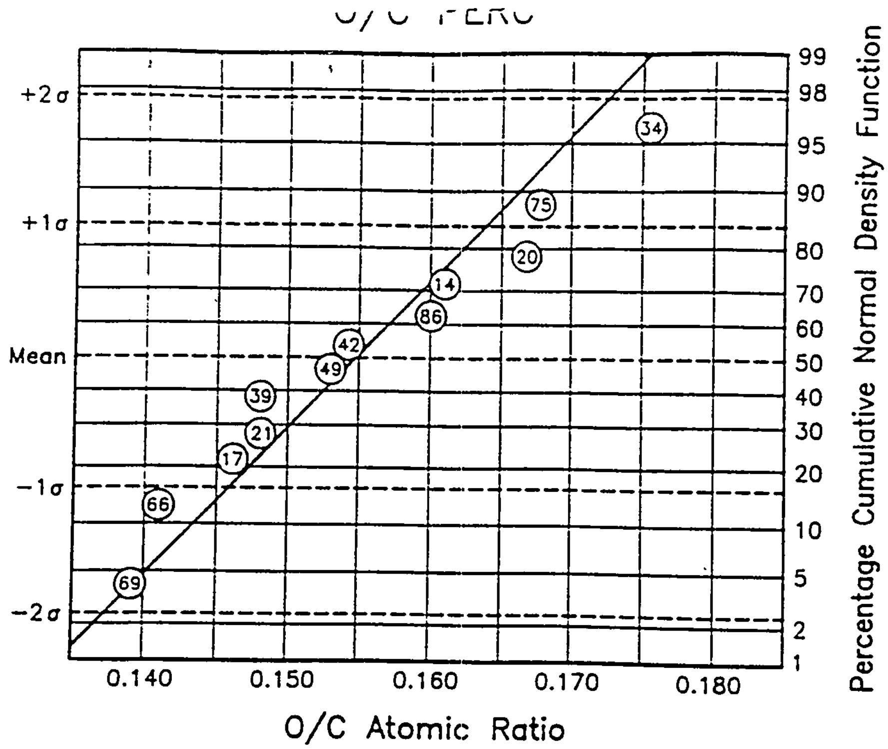


Figure 3 PERC oil O/C ratio plotted on normal probability distribution paper. Individual laboratory results shown as 69. The MPV (most probable value) distribution is given by the solid line.

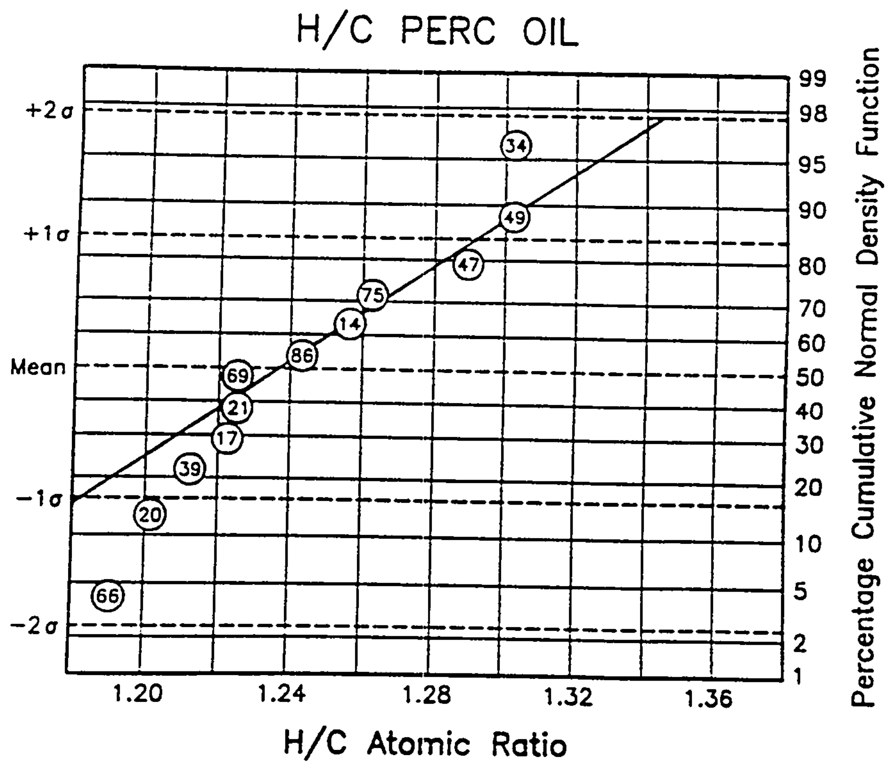


Figure 4 PERC oil H/C ratio plotted on normal probability distribution paper. Individual laboratory results shown as 69. The MPV (most probable value) distribution is given by the solid line.

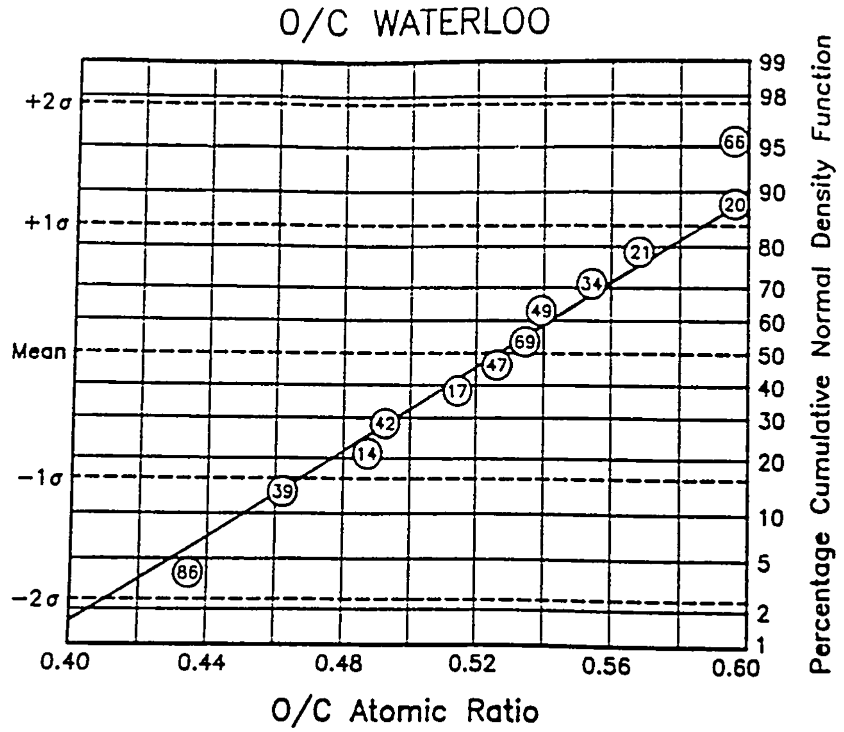


Figure 5 WFPP oil O/C ratio plotted on normal probability distribution paper. Individual laboratory results shown as 69. The MPV (most probable value) distribution is given by the solid line.

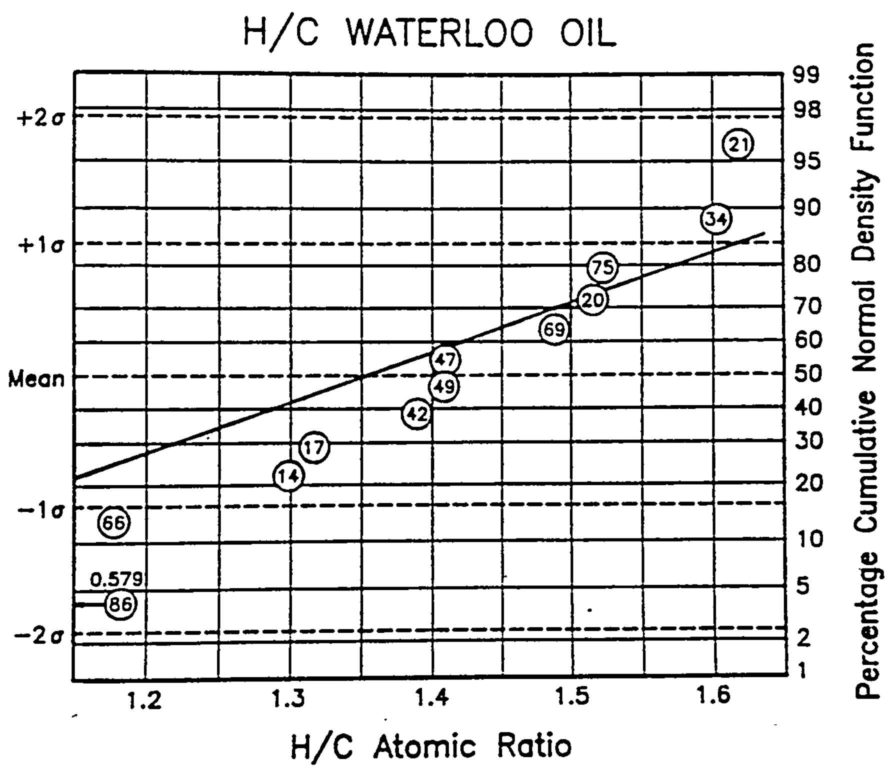


Figure 6 WFPP oil H/C ratio plotted on normal probability distribution paper. Individual laboratory results shown as 69. The MPV (most probable value) distribution is given by the solid line.

PROPERTIES AND CHARACTERISTICS OF ENSYN BIO-OIL

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PROPERTIES AND CHARACTERISTICS OF ENSYN BIO-OIL

1. Abstract

Bio-oil produced by ENSYN using the RTP method was examined for its physical, chemical and stability characteristics. Its pH, specific gravity, viscosity and water content were 2.8, 1.16, 98 cP and 21 wt% of bio-oil, respectively. The elemental content (by CHN analysis) of the oil was 49.8 wt% C, 7.5 wt% H, and 42.7 wt% O. No nitrogen was detected by the CHN analysis. Its flash point was 76 ^{o}C and vapor pressure over the temperature range 33-72 ^{o}C was between 5-39 kPa. Two other bio-oils produced by ENSYN under different conditions were also investigated for their phyisical properties.

Filtration (with screens, filter paper, fritted glass funnels) and separation (by centrifugation) showed that the bio-oil contained about 3.7 wt% char and 9.9 wt% tar. The ash (inorganics) content obtained from the char was 0.18 wt% and the total amount of ash in the bio-oil was 0.48 wt%.

The distillation characteristics of the bio-oil was studied at atmospheric pressure and under a vacuum of 172 Pa. The amount of distillate, up to 100 ^{o}C was 8.6 wt% of bio-oil, and at 108 ^{o}C, it was 25.0 wt% of bio-oil. The bio-oil consisted of 58.0 wt% low boiling fraction (<200 ^{o}C), 6.0 wt% high boiling fraction (200-450 ^{o}C) and 36.0 wt% non-volatiles (>450 ^{o}C). The distillate fractions were also analyzed using GC and GC/MS techniques.

The stability of the bio-oil was monitored by observing changes in its pH, density, viscosity and distillation characteristics over a 1 year period. The viscosity increased from 98 to 194 cP and the amount of distillate decreased. However, the pH and density remained almost unchanged.

Upon gradual addition of water, the bio-oil was found to separate (about 17 g of water per 100 g bio-oil) into two fractions: a water-soluble fraction (WSF) and an organic fraction, termed, pyrolytic Lignin Fraction (PLF). At pH=2.8 and 23 ^{o}C, the yield of PLF was 54 wt% of bio-oil. The yield of PLF and its viscosity was significantly affected by the pH and temperature of bio-oil.

The miscibility characteristics of diesel with Bio-oil (as is), Bio-oil:Solvent, PLF (as is) and PLF:Solvent (termed feeds) was investigated at room temperature and 45 ^{o}C. The solvents were methanol, ethanol and acetone. The estimated maximum amount of diesel (per 100 g of feed) required to obtain a stable miscibility for a test period of 24 h were: 16 g in bio-oil, 21 g in Bio-oil:Methanol (9:1), 25 g in Bio-oil:Ethanol (9:1), 19 g in Bio-oil:Acetone (9:1), 6.5 g in PLF:Methanol (9:1), 6.4 g in PLF:Ethanol (9:1) and 10.8 g in PLF:Acetone (9:1). Increasing the temperature to 45 ^{o}C or the amount of solvent resulted in decreased miscibility. Also, the miscibility of bio-oil with bunker C oil was investigated.

2. Introduction

The bio-oil produced by ENSYN uses the Rapid Thermal Processing (RTP) method [1,2] which is one of the fast pyrolysis technologies that are being developed to give high bio-oil yields. It consists of a number of reactor configurations and conditions which are employed to convert biomass to bio-oils. The bio-oil thus produced is a free flowing liquid with yields between 75-80 wt% of wood. Bio-oils from the RTP process are being considered for a number of potential applications. Some of the areas being considered include firing in utility electrical generating stations to replace fossil fuels, combustion in turbines or diesel engines, upgrading to produce hydrocarbon transport fuels or combustion additive to reduce emissions in coal fired systems, co-utilization within the traditional petroleum based infrastructure [2]. The success of the bio-oil in these applications require its thorough characterization. Earlier characterization work have been reported on oils from different reactor configurations which include RTP processes for fuels and for chemicals [1,3].

The objective of the current characterization was to determine the physical properties of the bio-oil, study its filtration, distillation, separation characteristics, stability nature and miscibility behavior with conventional fuels.

3. Physical Characteristics

Three different types of ENSYN bio-oil were investigated for their physical properties. These are referred to as Bio-oil A, Bio-oil B and Bio-oil C in this paper.

Bio-oil A was produced from commercial hardwood sawdust with the ENSYN RTP-3 Pilot Plant which was operated at approximately 525 ^{o}C and residence time of 450-500 ms.

Bio-oil B was produced from birch wood flour with ENSYN Research Unit (using reactor configuration RTP-3A) which was operated at approximately 515 ^{o}C and residence time of 500 ms. The bio-oil was hot filtered.

Bio-oil C was a commercial type bio-oil produced from commercial hardwood sawdust (Maple/Oak) with ENSYN 25 TPD Plant. The plant was operated at approximately 500 ^{o}C and residence time of 700 ms. The bio-oil was wet scrubbed.

The results are presented in Table 1 and are discussed below.

Elemental Composition by CHN Analysis:

The CHN content was performed with a Perkin Elmer 2000 CHN Analyzer. The oxygen content of the bio-oil was obtained by difference.

Comments:

The results show that the bio-oils were highly oxygenated in nature. No nitrogen was detected which is very favorable from environmental point of view.

Alkali and Ash content

The total ash content of the bio-oil was determined following the procedure outlined in ASTM D 482-80 for petroleum products [4]. The alkali content was determined by thermal ashing of the bio-oil followed by ICP-AES (i.e. Inductively Coupled Plasma-Atomic Emission Spectroscopy) method.

Comments:

The ash and alkali content of Bio-oil B were substantially lower than those of Bio-oil A. Especially, the calcium and potassium contents of Bio-oil B were much lower. However, the sodium content of Bio-oil B was still comparable to that of Bio-oil A. Also, the ash content of Bio-oil C is comparable with Bio-oil B. The alkali content of the bio-oil is suspected to be responsible for the production of ash during combustion.

Water content

The quantity of water in the oils were determined by Karl Fischer (KF) method. The procedure outlined in ASTM E 203-75 was followed [4]. With normal KF reagents the presence of aldehydes, ketones and carboxylic acids [5] in the bio-oil react with the KF titrant to produce water, thus, the amount of water is usually over-estimated. Instead, Hydranal-composite reagents, AQUASTAR Comp 5K and Solvent K were used for the titration. These reagents limit the water formed during titration.

Comments:

The bio-oils contained between 18 and 25 wt% water. Compared to petroleum fuels, the amount of water in the bio-oil was substantially high and therefore, the heating values of the bio-oils will be low. In order to improve the heating value, it may be necessary to dewater it.

pH

The pH of the bio-oil was determined with a Fischer Scientific Accumet Model 10 pH/mV meter equipped with controls and connections necessary to compensate automatically for effects of solution temperature and to standardize the meter with buffers.

Comments:

The bio-oils were highly acidic in nature. However, the pH of the Bio-oil B (2.45) makes it more acidic than Bio-oils A and C (pH of 2.8 and 2.66, respectively).

Flash Point.

The flash point of the bio-oil was determined following the procedure described in the ASTM D 93-80 method [4].

Table 1. Properties of bio-oils.

	BIO-OIL A	BIO-OIL B	BIO-OIL C
CHN Analysis			
C	49.8	43.0	49.7
H	7.5	7.2	7.6
N	0.0	0.0	0.0
O	42.7	49.8	42.6
Alkali Content, ppm			
Ca	500	8.6	
K	250	<0.5	
Na	50	40.0	
Water Content, wt%	21.2	25.0	18.0
Ash Content, wt%	0.48	0.06	0.10
pH	2.80	2.45	2.66
Surface Tension, mN/m	29.3	29.1	
Flash Point, °C	76	53	
Density, g/mL			
20 °C	1.210	1.217	1.243
30 °C	1.205	1.210	1.236
40 °C	1.199	1.202	1.225
50 °C	1.192	1.196	1.200
Kinematic Viscosity, cSt			
20 °C	81.0	30.4	1600
30 °C	49.8	14.9	546
40 °C	15.1	5.8	151
Vapor Pressure (VP), kPa	Temp., °C VP	Temp., °C VP	
	33.5 5.2	31.0 7.8	
	46.5 10.1	42.5 15.9	
	53.5 17.2	55.8 24.9	
	61.5 25.4	63.8 40.1	
	68.5 37.6	70.1 50.3	
	71.7 38.4	75.4 62.5	

Comments:

This is the lowest temperature at which vapors above the fuel ignite when exposed to a flame. Limits of the flash point must be determined for safe handling. Normally flash points above 50 °C are considered safe [6]. The flash point of Bio-oil B was lower than that of Bio-oil A (53 °C compared to 76 °C). Compared to diesel [7] (Flash point between 45 and 70 °C) the flash point of both oils fall within acceptable limits.

Density

The density measurements were made with a 10 mL pycnometer.

Comments:

The densities were higher than those for diesel (0.8-0.9 g/cc) but comparable with Bunker C oil (1.18 g/cc). With temperature, the densities changed only slightly.

Viscosity

The viscosity measurements were performed with a cone/plate Brookfield Digital Viscometer (Model DV-II).

Comments:

Among the three oils, the viscosity of Bio-oil B was the lowest. Those of Bio-oil C were exceptional high. The viscosity of Bio-oil B at 40 °C, 5.8 cSt is comparable to that of the summer grade Diesel of 3.0 cSt at 40 °C [6].

Surface Tension

The surface tension (ST) of the oil was measured with a Fisher Surface Tensiomat Model 21. The meter uses the Ring Method (platinum-iridium ring) to determine the surface tension. The instrument was calibrated with ethanol (ST=22.75 mN/m), acetone (ST=23.70 mN/m), and methanol (ST=22.61 mN/m).

Comments:

The surface tension of Bio-oils A and B were similar (29.3 and 29.1 mN/m, respectively). Compared to summer grade diesel (ST= 22.2 mN/m), the surface tension of the bio-oils were higher.

Vapor Pressure (VP)

As can be seen in Table 1 that at all the temperatures studied, the VP of the Bio-oil A was higher than those of Bio-oil B. It is required that the VP be low in order to minimize evaporative losses and emissions. Thus, with its high VP, the Bio-oil B is likely to be more volatile and also produce more emissions than the old bio-oil.

4. Bio-oil Filtration/Separation

Bio-oil A only was used for these studies. The filtration characteristics of the bio-oil was studied with screens and fritted glass filters and the separation characteristics was studied by centrifugation. The intent was to identify the most effective means of removing solid particles and to determine the amount of tar in the bio-oil. Also, attempts were made to approximately determine the size distribution of the particulates present in the bio-oil. The effect of temperature on the filtration behavior with the three techniques given above were also investigated.

The bio-oil was considered to consist of the clean oil (filtrate), tar and solid particulates (i.e. char and ash (inorganics)). The results are discussed below.

Filtration by Fritted Glass Filters

Fritted glass funnels with filters of pore sizes 4-5.5 (fine), 10-15 (medium) and 40-60 μm (coarse) were used. Each was 30 mL in volume and the filter disc was 10 mm ID and 3 mm thick. Attempts to filter the bio-oil at atmospheric pressure and room temperature failed. Thus, at atmospheric pressure, filtration was carried out at 50 ^{O}C. In order to reduce the filtration time, similar filtration tests were performed under vacuum (0.4 mmHg) and at room temperature (24 ^{O}C) and 50 ^{O}C. The results of these tests are given in Table 2.

As expected, the fine filter provided the best removal of particulates. About 3.69 wt% char and 10.24 wt% tar were separated from the bio-oil at room temperature compared to 3.36 wt% char and 9.66 wt% tar at 50 ^{O}C. The ash content of the char was 0.19 wt% of bio-oil in both cases. This char constituted about 40 wt% of ash in the bio-oil. This meant that about 60 wt% of ash were of particle sizes less than 4 μm and were retained in the filtrate.

Most of the particulates were retained on the coarse filter. For instance, at 24 ^{O}C, 36 wt% of the ash, 91 wt% of the char and 68 wt% of the tar were retained on the coarse filter indicating that most of the particulates were of sizes greater than 40 μm.

Table 2: Atmospheric pressure and vacuum filtration of bio-oil with fritted glass funnels.
Basis: 100 g bio-oil

Filter Size, μm	Temperature, ^{o}C	Filtration Time, min	[1]Ash, g	Char, g	Tar, g	Filtrate, g
Filtration at Atmospheric Pressure						
10-15	50	2940	0.19	3.5	11.79	84.71
40-60	50	1740	0.16	3.01	11.26	85.73
Filtration under Vacuum (0.4 mmHg)						
4-5.5	24	180	0.19	3.69	10.24	86.07
	50	72	0.16	3.36	9.66	86.99
10-15	24	55	0.16	3.46	7.47	89.07
	50	23	0.15	3.09	6.50	90.41
40-60	24	40	0.15	3.36	6.96	89.68
	50	7	0.15	3.02	6.50	90.48

[1]Ash: Ash content of char fraction only (Fraction is based on 100 g bio-oil). The ash content of the whole bio-oil was 0.48 wt%.

Filtration by Screening

Screen of sizes 45 (325 mesh), 53 (270 mesh), 75 (200 mesh) and 150 μm (100 mesh) were used. They were 3 in. in diameter. About 3.45 (24 °C) and 3.34 g (50 °C) char were separated from the bio-oil.

The size distribution with the screens showed that most of the char particles were of sizes between 45 to 53 μm indicating that filters of pore sizes less than 53 μm would be required for effective removal of particulates.

Separation by Centrifugation

The results obtained from centrifugation of the bio-oil are given in Table 3. It is seen that an optimum of 0.13 wt% ash, 3.60 wt% char and 9.9 wt% tar were separated from the bio-oil at room temperature. At 50 °C, up to 0.18 wt% ash, 3.65 wt% char and 7.72 wt% tar were separated from the bio-oil. A speed of 1.15×10^4 rpm (RCF 9.98×10^3) was sufficient to achieve optimum separation. This speed falls within the range for industrial centrifuges.

Table 3. Separation of ENSYN bio-oil by centrifugation.
Basis: 100 g bio-oil, Filtration time, 20 min.

Speed, rpm	Relative Centrifugal Force, g	Ash, g	Char, g	Tar, g
24 °C				
1.45×10^4	1.60×10^4	0.13	3.60	9.84
1.15×10^4	9.98×10^3	0.13	3.58	9.90
9.2×10^3	6.39×10^3	0.11	3.47	9.68
5.52×10^3	2.30×10^3	0.08	3.20	8.92
2.4×10^3	4.30×10^2	0.07	2.58	5.08
50 °C				
1.45×10^4	1.60×10^4	0.18	3.65	7.40
1.15×10^4	9.98×10^3	0.16	3.65	7.72
9.2×10^3	6.39×10^3	0.16	3.59	7.32
5.52×10^3	2.30×10^3	0.13	3.26	6.61
2.4×10^3	4.30×10^2	0.05	2.30	4.00

Considering the three methods discussed above, the results indicated that centrifugation was the best method for removal of particulates from the bio-oil. Centrifugation provided one of the best methods of particulate removal in relatively less time. Also, after the particles have been removed by centrifugation, viscosities of the clarified bio-oil were comparable with those of the parent bio-oil. In addition, it had an advantage of retaining a higher amount of tar in the product. This was preferable because it allowed more organic material in the clarified bio-oil which is favorable from heating value point of view. Losses were also minimal.

The results also show that filtration/separation at 50 °C was better than at room temperature.

5. Bio-oil Distillation Characteristics

The distillation characteristics of the bio-oil were studied at atmospheric pressure and at vacuum pressure conditions. Distillation at atmospheric pressure was carried out in order to investigate the extent of volatility of the bio-oil under normal conditions of temperature and pressure as well as to determine the composition of the volatile portion of bio-oil. The vacuum distillations were performed in order to determine the fraction of non-volatile residue (or volatile fraction of bio-oil). Since it was difficult to determine the composition of bio-oil (as is) directly, GC-MS analysis of the volatile fractions were used as means of determining the chemical composition of the bio-oil. The results are discussed below.

Distillation at Atmospheric Pressure

The distillation characteristics were studied following the procedure described in Standard Method IP 24 for distillation of crude petroleum [7].

The amount of volatiles obtained at each cut temperature are presented in Table 4 and the composition of the volatile fractions at selected cut temperatures can be found in Table 5. A list of the main components of the volatile fractions are given in Table 6.

Based on 100 g bio-oil, the first distillate drop was obtained at approximately 49 ^oC. The amount of bio-oil which was obtained at a cut temperature of 100 ^oC was 8.49 wt%. It is interesting to note that most of the water contained in the bio-oil evaporated between 108 and 115 ^oC. This observation is indicative of the phenomenon of boiling point elevation of a volatile solvent (or liquid) which results when one or more involatile solute are dissolved in the volatile solvent (or liquid). The pH of the volatile fractions was 2.56 at 73 ^oC and increased to 2.80 at 100 ^oC indicating that the volatile fraction was highly acidic in nature.

Table 4. Distillation of bio-oil at atmospheric pressure.
Atmospheric pressure, 751.6 mm. Hg, Basis: 100 g bio-oil

Fraction No	Cut Temp. ^oC	Wt%	Sum wt%	pH	[1]Water Content wt%	Amount of Water, wt%
1	23	0.05	0.05			
2	35	0.04	0.09			
3	49	0.04	0.13			
4	58	0.06	0.19			
5	65	0.35	0.54		32	0.2
6	73	0.58	1.12	2.56	55	0.6
7	80	0.91	2.03	2.58	71	1.4
8	95	2.64	4.67	2.62	80	3.7
9	100	3.82	8.49	2.80	85	7.2
10	108	13.6	22.10	2.83	85	18.8
11	115	5.50	27.60	2.94	80	22.1
12	130	4.50	32.10	2.94	70	22.5
13	150	2.00	34.10	2.94	68	23.1

[1]wt% of the volatile product (condensate).

Table 5: Chemical composition (wt% of volatile fraction) of volatile fractions.

	Distillation Temperature Range, ^oC				
Composition	Fraction 5 Up to 65	Fraction 6 66-73	Fraction 7 74-80	Fraction 8 80-95	Fraction 9 96-100
Acids (and Esters)	47.2	34.5	22.5	14.5	9.0
Alcohols	1.9	---	---	---	---
Aldehydes	1.0	0.9	0.7	0.6	1.0
Aliphatic Hydrocarbons	8.6	2.5	2.3	1.9	2.4
Amines	0.4	---	---	0.1	0.2
Aromatic Hydrocarbons	---	---	---	---	---
Ethers	---	---	---	---	---
Furans	1.7	0.5	0.2	0.6	0.6
Ketones	---	---	---	---	---
Phenols	0.1	0.9	0.4	0.3	0.9
Unidentified Fraction	7.1	5.7	2.9	2.0	0.9
Water	32.0	55.0	71.0	80.0	85.0
Total	100	100	100	100	100

Table 6. Main components of the volatile fractions.

Acids and Esters Ethanethioic acid, (methyl) ester- Hexanoic acid, 2-methyl-3-oxo-, ethyl ester- Acetic acid Butanoic acid, 3-hydroxy- Propanoic acid Ethanoic acid, dibutyl ester-	**Aliphatic Hydrocarbons:** Propane, 2,2-dimethyl- Cyclobutene, 1,2,3,4-tetramethyl-, cis
Alcohols 2-Propanol, 1-(diethylamino)-	**Furans:** Furan, 2,5-dimethyl-
Aldehydes: 2-Furancarboxyaldehyde Furancarboxyaldehyde, 5-methyl-	**Phenols:** Phenol, 2-methoxy-

The volatile fraction was composed of water and various organic compounds. Of the organic compounds, organic acids and esters were the main components. It was 47.2 wt% of the volatile fraction at a cut temperature of 65 °C (Fraction 5) and decreased with temperature to 9.0 wt% at 100 °C (Fraction 9). Propanoic acid, 3-hydroxy butanoic acid, and dibutyl ester of ethanoic acid were the main components. The next major group of compounds was aliphatic hydrocarbons which ranged from 8.6 wt% of the volatile fraction at 65 °C to a minimum value of 1.9 wt% at 97 °C (Fraction 8). Only small fractions of alcohols, aldehydes, amines, furans and phenols were identified. No aromatic hydrocarbons, ketones or ethers were identified.. The presence of high amounts of organic acids and esters of organic acids may be the reason for high acidity (pH between 2.56 and 2.80) of the volatile fractions. Also, these acidic compounds may be the main cause of the high acidity of the bio-oil (pH of 2.8).

Vacuum Distillation

In order to determine the amount of non-volatile residue (and volatiles) while minimizing thermal decomposition, samples of bio-oil were distilled under vacuum (172 Pa) at 23, 150, 200 and 250 °C using a Buchi GKR-50 Distillation Unit. The results are presented in Table 7. Using Bio-oil A, the amount of residue decreased with temperature and ranged between 27.7-89.6 wt% of bio-oil. In order to determine the composition of Bio-oil A, the organic distillate fraction obtained at 200 °C was used for detailed analysis (GC-MS analysis). The results are presented in Table 8. Over 100 different compounds were present. Acetic acid, propanoic acid, phenol, alkylated phenols and cresols were some of the main components. Ketones were by far the most abundant components, followed by acids and esters, aldehydes and phenols, alcohols, hydrocarbons and furans. Similar compositions have been reported by other researchers [8,9].

Table 7. Vacuum distillation characteristics of bio-oil.

Temp. °C	Vacuum Distillation (Amount, wt% of bio-oil)					
	Distillate			Residue		
	Bio-oil A	Bio-oil B	Bio-oil C	Bio-oil A	Bio-oil B	Bio-oil C
23	10.4	16.6	17.6	89.6	83.4	82.4
150	54.6			45.4		
200	63.4	68.4	48.3	36.6	31.6	51.7
250	72.3			27.7		

Table 8. Composition (wt% of organic distillate fraction) of organic distillate fraction (at 200 °C, 172 Pa from Bio-oil A).

Acids and Esters	10.4
Alcohols	5.3
Aldehydes	10.9
Aliphatic Hydrocarbons	0.4
Amines	0.5
Aromatic Hydrocarbons	5.6
Ethers	2.2
Furans	2.5
Ketones	36.6
Phenols	10.9
Unidentified Fraction	14.7
Total	100.0

6. Stability behavior of Bio-oil

Bio-oil A was used for the stability studies. The stability of the bio-oil was examined by monitoring the changes in its density, viscosity, pH and distillation characteristics over a 1 year period. The results of these studies are presented in Table 9.

The main changes were observed in the viscosity and the distillation characteristics of the bio-oil. The pH and density of the bio-oil remained almost unchanged with time.

The viscosity increased with time from 84.5 to 162.3 cSt after 1 year. The increase in viscosity was very drastic over the first few months (up to about 4th month) and thereafter it appeared to taper off.

The amount of distillate obtained from vacuum distillation also decreased from 63.4 to 60.8 wt% of bio-oil and the amount of the volatile fraction obtained at 100 °C (distillation at atmospheric pressure) decreased from 8.49 to 7.99 over a 9 month period. These results show that the bio-oil appeared to be unstable initially but its stability appeared to improve over time. The most drastic changes occurred in the viscosity of the oil.

Table 9. Changes in bio-oil properties with time.
(Properties were measured at 25 °C)

Month	Density	Viscosity		pH	Distillation	
	g/mL	cP	cSt		[1]Vacuum	[2]Atmospheric
1	1.16	98	84.5	2.82	63.4	
2	1.16	134	115.5	2.80		
3	1.17	154	131.6	2.80	61.9	8.49
4	1.18	169	143.2	2.80		
5	1.18	178	150.8	2.80	61.3	
6	1.18	185	156.8	2.80		8.00
8	1.18	188	159.3	2.80	61.0	
10	1.18	192	162.7	2.80		
12	1.18	192	162.3	2.80	60.8	7.99

[1]Amount of distillate obtained at 200 °C, 172 Pa
[2]Amount of volatiles obtained at 100 °C

7. Separation of Bio-oil Into Pyrolytic Lignin Fraction (PLF) and Water Soluble Fraction (WSF)

The bio-oil contained 21 wt% water which is not desirable from the combustion point of view. Therefore, it was decided to separate the water from the oil. By adding water, it was possible to separate the water in the bio-oil leaving an organic fraction (termed Pyrolytic Lignin Fraction, (PLF)). A minimum of about 17 g water per 100 g bio-oil was needed to cause this separation. The results of this separation with increasing temperature is presented in Table 10. Bio-oil A was used for detailed studies and the results obtained are discussed below.

An optimum of 58.0 wt% PLF was obtained at 50 °C compared to 54.0 wt% at 23 °C and 38.5 wt% at 80 °C. Interestingly, the viscosity of the PLF obtained at 50 °C was much lower than those obtained at 23 and 80 °C. Overall, the viscosities were exceptionally high compared to that of the original bio-oil. Also, the PLF fractions barely flowed.

Attempts were made to optimize the yield of PLF by adjusting the pH of the bio-oil. In order to do this, inorganic (saturated NaOH) and organic (n-butylamine) bases were added to the bio-oil to adjust the pH before separation with water. With NaOH, an optimum of 62.8 wt% PLF was obtained at pH=4.00. With n-butylamine, the yield of PLF was a maximum 64.0 wt% at pH=5.22. Thus, by increasing the pH of the bio-oil, it was possible to increase the yield of PLF to some extent.

The high viscosities of the PLF imply that they cannot be used directly in most applications and as such need to be solubilized before usage. The PLF was readily soluble in ketones (such as acetone) and alcohols (such as methanol, ethanol and isopropyl alcohol). When 9 parts of PLF were added to 1 part of solvent, (i.e., acetone, methanol and ethanol), the viscosity of PLF was found to decreased dramatically to between 49-51 cSt (at 20 °C) and the pH was between 3.20-3.40 compared to 2.80 of the original bio-oil. However, the PLF was sparingly soluble in both aliphatic (such as hexane and octane) and aromatic hydrocarbons (such as xylene, toluene, tetralin), and ethers (such as anisole and petroleum ether). Thus, to make the PLF flow, small amounts of ketones or alcohols could be added to it.

The PLF consisted of about 47 wt% volatile and 53 wt% non-volatile fraction (vacuum distillation at 200 °C, 172 Pa). The non-volatile fraction contained almost all the char. The elemental compositions (Table 10) show that the carbon content of the PLF increased (oxygen content decreased) as the separation temperature was increased.

The composition of the WSF fractions obtained at room temperature and at 80 °C are given in Table 11. The WSF consisted mostly of acids and esters (10-13 wt% of WSF), alcohols (3-12 wt%), ketones (5-17 wt%), aldehydes (2-6 wt%), ethers (1-32) and phenols (7-13 wt%). The hydrocarbon content was negligible. It is interesting to note that the ether fraction increased substantially when the temperature

was increased from room temperature to 80 ^{o}C. Propanoic acid, 2-propanol, 1-ethoxyheptane, 2-methoxyphenol and 3-methyl-2-Cyclopenten-1-one were some of the major compounds. The composition varied significantly with temperature.

Table 10. Yields of PLF and WSF and their physical properties.

		Amt., wt%	Density, g/mL	Viscosity, cP		CHN Analysis		
				20 ^{o}C	50 ^{o}C	Carbon	Hydrogen.	Oxygen
Separation at 23 ^{o}C								
Bio-oil A	[1]PLF	54.0	1.20	28000	1050	42.7	6.5	50.8
	[2]WSF	46.0	0.96	6				
Bio-oil B	PLF	41.2						
	WSF	58.8						
Bio-oil C	PLF	82.0				53.0	8.0	39.0
	WSF	46.0						
Separation at 50 ^{o}C								
Bio-oil A	PLF	58.0	1.20	9770	770	50.5	6.9	42.6
	WSF	42.0	0.96	6				
Bio-oil B	PLF	24.5						
	WSF	75.5						
Bio-oil C	PLF	78.5				53.3	7.6	39.1
	WSF	21.5						
Separation at 80 ^{o}C								
Bio-oil A	PLF	38.5	1.23	20000	880	60.7	6.3	33.0
	WSF	61.5	0.96	6				
Bio-oil B	PLF	24.3						
	WSF	75.7						
Bio-oil C	PLF	76.0				53.8	7.5	38.7
	WSF	24.0						

[1]Pyrolytic Lignin Fraction. [2]Water-soluble Fraction

Table 11. Composition of the Water Soluble Fraction of bio-oils.

	Bio-oil A		Bio-oil B	
Functional Group / Temperature, ^{o}C	23	80	23	80
Water	21.0	21.0	25.0	25.0
Acids and Esters	10.2	12.7	11.5	11.8
Alcohols	12.1	0.5	11.6	2.8
Aldehydes	6.1	1.5	5.8	2.1
Aliphatic Hydrocarbons	0.9	0.7	1.1	0.6
Amines	5.2	0.2	4.2	1.1
Aromatic Hydrocarbons	-----	0.6	0.5	0.8
Ethers	1.0	32.3	3.4	24.3
Furans	3.8	1.5	3.9	3.3
Ketones	16.7	5.1	16.5	10.8
Phenols	12.6	7.3	12.1	10.6
Unidentified Fraction	13.2	16.6	4.4	6.8
Total	100	100	100	100

8. Miscibility of Bio-oil, PLF, Bio-oil-solvent and PLF-Solvent with Diesel and Bunker C

In order to identify how the bio-oil could be utilized within the traditional petroleum based fuels infrastructure, the miscibility of the bio-oil with diesel and bunker C (as sources of fuel oils) were investigated. A number of studies were performed which included the following. First, the miscibility of bio-oil (as is) with diesel and bunker C was studied. Secondly, the bio-oil was mixed in different proportions with solvents (methanol, ethanol and acetone) and its miscibility with diesel and bunker C was investigated. In order to examine changes in the miscibility associated with temperature, the experiments

were conducted at room temperature (23 ^{o}C) and at 45 ^{o}C. Similar miscibility studies were also performed with the PLF.

The Bio-oil+Solvent and PLF+Solvent mixtures used were prepared in the weigh ratios; 9:1, 4:1 and 1:1. The changes in the miscibility behavior with time, amount of diesel or bunker C which was permanently miscible with feed at different proportions as well as the density, viscosity and pH of the miscible fractions were monitored. The results are discussed below.

Miscibility with Diesel

1. General Comments:

The Bio-oil or Bio-oil+Solvent mixtures were miscible with diesel to various extents. The miscibility depended on the viscosity, temperature, as well as the amount of solvent. The miscibility decreased with temperature as well as with the amount of solvent added to bio-oil. Also, it decreased when the viscosity of the Bio-oil+Solvent mixture decreased.

Centrifuging the bio-oil before mixing with diesel resulted in decreased miscibility. The reduced miscibility may be due to decreased viscosity or the higher water content of centrifuged bio-oil compared to original bio-oil. Increasing the temperature from 23 to 45 ^{o}C appeared to reduce the time for stable miscibility. Also, the amount of diesel contained in the miscible fractions was slightly reduced. Thus, although the viscosity of the mixtures were lower with temperature increase, the miscibility of diesel in the feed decreased also. Increasing the amount of solvent resulted in increased pH, reduced viscosity and density. On the other hand, the miscibility and stability of the miscible fractions decreased. In addition, the amount of diesel permanently miscible in the feed decreased. It was interesting to note that as the amount of diesel which was permanently miscible in the feed increased, in most cases, the viscosity of the resulting mixture also increased.

In Table 12, the miscibility of Bio-oil (as is) with diesel is given as an illustration.

The miscibility of Bio-oil+Diesel (9:1 weight ratio) mixture was stable for up to about 4 h. After 4 h, a layer of diesel was formed indicating separation or breakdown of miscibility. On the other hand, some amount of the diesel remained "permanently" in the bio-oil. As the amount of diesel was increased, the extent (time for stable miscibility) of the miscibility decreased. At a ratio of 6:4 the two fractions were clearly immiscible. A maximum of about 16 g diesel per 100 g bio-oil was found to be permanently miscible with the bio-oil.

Table 12. Miscibility of Bio-oil (B) with Diesel (D).
Stirring speed: 1500 rpm; Stirring Time: 30 min

B:D Wt. Ratio	Miscibility at Room Temperature, 23 ^{o}C	[1]Amt	Miscibility at 45 ^{o}C
9:1	* Miscible foe about 4 h * Small diesel layer visible after 4 h * Small diesel layer after 24 h	10.0	Same as at room temperature
8:2	* Miscible for 2-3 h * Small diesel layer after 3 h * Small diesel layer after 24 h	16.0	Same as at room temperature
7:3	* Miscible for about 1 h * Separation developed after 1 h Large layer of diesel	16.0	* Miscible for about 30 min * Separation developed after 30 min
6:4	* Not completely miscible * Pockets of bio-oil and diesel observed during stirring * Separation developed immediately after stirring.	---	Same as at room temperature
5:5	Same as 6:4	---	Same as 6:4
4:6	No miscibility observed	---	Same as 4:6
3:7	Same as 4:6	---	Same as 4:6
2:8	Same as 4:6	---	Same as 4:6
1:9	Same as 4:6	---	Same as 4:6

[1]Amt: Maximum amount (g) of diesel per 100 g bio-oil required to obtain stable miscibility.

2. Optimum Miscibilities

The best proportions of feed (Bio-oil or Bio-oil+Solvent or PLF+Solvent) and diesel required to obtain optimum miscibility as well as the amount of diesel which remained permanently miscible in the feed are summarized in Table 13.

Table 13. Summary of ratios of Feed+Diesel required to obtain best miscibility and the optimum amount of diesel permanently retained in the miscible fraction.

Feed	Optimum Wt. Ratio of Feed to Diesel	Optimum Amount of Diesel per 100 g Bio-oil
Bio-oil	8:2	16.0
Centrifuged Bio-oil	8:2	10.4
Bio-oil:Methanol (9:1)	7:3	21.0
Bio-oil:Ethanol	7:3	25.0
Bio-oil:Acetone (9:1)	8:2	19.0
PLF:Methanol (9:1)	9:1	6.5
PLF:Ethanol (9:1)	9:1	6.4
PLF:Acetone (9:1)	8:2	10.8

Miscibility with Bunker C

The miscibility studies were carried out by mixing the bio-oil (or Bio-oil+Solvent) and bunker C and stirring for 30 min. On account of the high viscosity and dark color of both bio-oil and bunker C, extra measures were taken in order to study the nature of the miscibility. These are described below:

After stirring for 30 min, two sample of the Bio-oil or Bio-oil+Solvent and Bunker C mixture were taken. One sample was placed in a watch glass and the other in a test tube of diameter 5 mm. The sample in the watch glass was allowed to spread and it was examined for uniformity or homogeneity with the aid of a light source. Similarly, the sample in the test tube was examined with the light source. Usually, non-homogeneity or poor miscibility was indicated by the presence of globules of bio-oil in bunker C or vice versa. The absence of globules was viewed as an indication of uniform miscibility.

At room temperature, Bio-oil A was miscible with bunker C at all proportions. The miscibility was stable for over 24 h and extended into days. However, the viscosity of these mixtures appeared to be exceptionally high.

Bunker C was immiscible with ethanol and methanol. As a result, the Bio-oil+Ethanol and Bio-oil+Methanol with bunker miscibilities were exceptionally poor. On the other hand, bunker C was readily miscible with acetone. Hence, the miscibility of Bio-oil+Acetone and bunker C was exceptionally good. In Table 14, the miscibility behavior has been summarized for this system. The results showed that acetone can be added to the Bio-oil+Bunker C mixtures in order to reduce the viscosity and make it more fluid while maintaining long miscibility times in the order of hours.

Compared to diesel, the bio-oil was more miscible with bunker C than with diesel.

Table 14. Miscibility of Bio-oil A+Acetone (B+A) and Bunker C (C).

B+A:C Weight Ratio	Observation
	Room Temperature, 23 °C
Bio-oil:Acetone Ratio = 9:1	
9:1	Miscible up to about 24 h
7:3	Miscible up to about 6 h
5:5	Miscible up to about 6 h
3:7	Miscible up to about 6 h
1:9	Miscible up to about 24 h
Bio-oil:Acetone Ratio = 4:1	
9:1	Miscible up to about 24 h
7:3	Miscible up to about 4 h
5:5	Miscible up to about 4 h
3:7	Miscible up to about 6 h
1:9	Miscible up to about 24 h
Bio-oil:Acetone Ratio = 1:1	
9:1	Miscible up to about 3 h
7:3	Miscible up to about 3 h
5:5	Miscible up to about 3 h
3:7	Miscible up to about 3 h
1:9	Miscible up to about 3 h

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Storage of Biomass Pyrolysis Oils

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An important advantage of liquid fuels is their storability. Storage procedures for petroleum fuels are well established. However, they cannot be directly applied to biomass pyrolysis oils because of significant differences in the physical/chemical properties of those liquids. Biomass pyrolysis oils are not yet standardized products and can exhibit a range of properties depending on the pyrolysis technology employed, process conditions, and feed materials. Nevertheless, they all contain components that can react to form higher molecular weight species. The oils are also corrosive to common storage tank construction materials (mild steel). Reactions between oil components and between the oil and tank materials are unfavorable and should be prevented (or at least minimized).

This paper describes how oak pyrolysis oil changes physically and chemically when stored under various conditions. The oils were generated in the National Renewable Energy Laboratory (NREL) vortex reactor system. Throughout the study which included temperature and time conditions, the oil remained in a single phase, and its pH was not affected by storage. However, the water content, viscosity, and molecular weight of the oil increased with time and the temperature of storage. The changes in the weight-average molecular weight and viscosity of the oil were successfully correlated using first order kinetics. The proposed method can be useful in estimating the influence of storage conditions on oil properties.

Other works demonstrated that carbon steel and aluminum are strongly corroded by wood pyrolysis oils, even at moderate temperatures. In this study, polyester resin and polyethylene, potential materials for constructing oil storage tanks, were evaluated for chemical resistance to oak pyrolysis oil. Only a slight swelling, less than that allowed by the standards, was observed in both materials which were exposed to the oil at 20° C and 60° C.

1. Introduction

Since the 1980s, several fast pyrolysis processes for converting biomass into liquid products have been developed. At least three of them are in use currently at the stage of a pilot plant or a process demonstration unit. These units are able to generate oils that have the potential to be used as a fuel oil substitute or as a source of chemicals. For any of the applications, the oils need to be properly stored. Storability and transportability are considered to be major advantages of the oils over the producer gas generated by gasification processes. However, storage procedures for biomass oils have not been established yet.

It is well known that pyrolysis oils contain many components that can react between themselves to form higher molecular weight species. In general, these reactions result in an increase in viscosity and a corresponding decrease in volatility, both unfavorable for fuel applications. Therefore, it is very important for any potential user to know how storage conditions effect the properties of these oils and what can be done to minimize the extent of these changes. The stability of biomass pyrolysis oils has not been extensively studied, and the only data published to date are those of Knight et al. [1] for a Tech-Air process oil. However, the oils generated by more efficient fast pyrolysis processes can behave differently than the updraft gasifier oil from Tech-Air. The NREL work on stability of fast ablative pyrolysis wood oil by Czernik et al. [2] will be published shortly.

The other important aspect for storing the oils is the compatibility of materials to be used for construction of tanks. Biomass pyrolysis oils were found to be corrosive to common construction materials such as carbon steel and aluminum. Data on the corrosion rate of metals by pyrolysis oils were published by Soltes and Lin [3] and by Aubin and Roy [4]. Other potential tank construction materials - polymers -were tested in this work.

2. Changes of Properties of Pyrolysis Oils During Storage

2.1. Experimental

The oil used in this study was generated by the pyrolysis of oak wood in the NREL vortex reactor system. The technology used, called fast ablative pyrolysis, was described by Diebold and Scahill [5]. The oil contained 16.1% water, 14.1% fixed carbon, and 0.05% ash. The elemental composition of the oil was 46.3% carbon, 6.8% hydrogen, 46.8% oxygen, and 0.1% nitrogen, corresponding to 55.6% carbon, 5.0% hydrogen, 39.3% oxygen, and 0.1% nitrogen on a moisture-free basis. The oil had a pH 2.9, a density of 1.29 g/cm^3, and a viscosity (at 40° C) of 159 cP. Following the principles of statistically designed experiments, the oil samples were stored for selected time periods at 37° C, 60° C, or 90° C. The samples were stored at 37° C for as many as 12 weeks, at 60° C up to 9 days, and at 90° C up to 15 hours.

The visual observation of the oil after storage indicated that the oil samples remained homogeneous throughout the experiment. Certain properties such as pH, water content, and viscosity were measured for the stored oil samples. Structural changes in the oil were also studied using gel permeation chromatography (GPC).

The pH of the oil samples was measured at room temperature using a Sentron Model 2001 pH System with an Ion Sensitive Field Effect Transistor as a sensor. The precision of the measurements was estimated at 0.1 units.

The water content of the oil samples was determined by Karl-Fischer titration using a Metrohm 701 titrator and Hydra-Point Comp 5 titrant (from Baker). The precision of the measure-ment is estimated to be ±0.2% in the studied concentration range.

The viscosity for the oil samples was measured using a Brookfield Digital Viscometer Model LVTD. This instrument measures the torque necessary for the rotating element to overcome the resistance of the fluid, which is proportional to viscosity. The precision of the measurement is ±2% because of variations in fluid temperature. The values were measured at five temperatures and then linearly correlated using the variables log viscosity and 1/T (the correlation coefficient r^2 was always greater than 0.99).

The molecular weight distribution of the oil samples was determined by gel permeation chromatography (GPC) using a Hewlett-Packard HP 1090 high-performance liquid chromatograph with an ultraviolet diode-array detector. The separation was done using two columns in series: Polymer Laboratories PL Gel 100 Å pore size and 10 μm particle diameter, and Altex μ-Spherogel 1000 Å pore size and 10 μm particle diameter. Both columns were 390 mm long and had an 8 mm diameter. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1 ml/min. Oil samples were dissolved in THF at a concentration of 2 g/l. Elution times were converted to apparent molecular weight by calibration with polystyrene standards.

2.2. Results and Discussion

The pH values for all samples of the stored oil were in the range of 2.9-3.1. They were randomly scattered, and no effects of storage on the pH of the oil were observed within the experimental error.

The water concentration in the oil increased with the length of storage. This increase was smaller for the samples stored at 37°C, even after extended storage time. Higher storage temperatures resulted in greater changes in water content. The results are presented in Table 1.

Table 1. Water Content of Stored Pyrolysis Oil

37°C		60°C		90°C	
Time days	Water wt%	Time days	Water wt.%	Time days	Water wt.%
0	16.1	0	16.3	0	16.2
7	16.2	1	16.3	1	16.2
17	16.6	2	16.6	2	16.6
28	16.5	3	17.1	4.5	17.3
56	16.6	6.7	17.7	8	17.5
84	16.6	9	17.7	15	17.7

The release of water suggests that some condensation or dehydration reactions occurred in the oil during storage, especially when exposed to higher temperatures.

The viscosity of the oil increased with the length of storage. The changes resulting from storage at higher temperatures were greater than those occurring at 37° C. The increase in the oil viscosity after almost 3 months of storage at 37° C was equivalent to that after approximately 4 days at 60° C or to 6 hours at 90°C. The results of the measurements are presented in Table 2. The viscosity of pyrolysis oils strongly depends on their water content. Normally dilution with water makes the oils less viscous. However, the increase in water concentration of the stored oil was accompanied by an increase in its viscosity. Because viscosity is related to the molecular weight of the material, these measurements indicate that condensation reactions have occurred in the oil, especially when exposed to higher temperatures.

The molecular weight distributions of the oil samples exhibited a paucidisperse behavior (multiple components). Figure 1 shows that with increasing time in storage, the proportion of low-molecular-weight material decreased while that of high-molecular-weight material increased. This effect is more distinctive for the oil samples stored at higher temperatures.

Table 2. Viscosity of Stored Pyrolysis Oil

37°C		60°C		90°C	
Time days	Viscosity cP	Time days	Viscosity cP	Time hours	Viscosity cP
0	152	0	154	0	144
7	165	1	183	1	152
17	169	2	220	2	167
17	172	2	214	2	164
28	201	3	226	4.5	210
56	252	6.7	321	8	286
84	268	9	363	15	326
84	258	9	360	15	309

The increase in the amount of the high-molecular-weight fraction resulted in an increase in the average molecular weight (M_w) of the stored oil. The molecular weight of the oil increased faster during the initial period of storage at higher temperatures and then tended to level off. The values of the molecular weight of the stored oil are presented in Table 3.
The results confirmed that polymerization/condensation occurred during storage as suggested by the changes in viscosity of the stored oil. Similarly to the viscosity measurements, the weight-average molecular weight increase obtained after storage for 12 weeks at 37°C was comparable to the increase that occurred after 4 days at 60°C or 6 hours at 90°C.

2.3. Correlation of changes in stored pyrolysis oil

Changes in the oil properties are caused by chemical reactions occurring during storage. However, the kinetics of these processes is very difficult to study because of the great number of components that can react with different rates. A measurement of the total reaction progress is the increase in the molecular weight of the oil as determined by the GPC analyses. Based on leveling-off of the average molecular weight in the stored oil, conversion (α) was defined as the ratio of the actual increase in the weight-average molecular weight of the stored oil to the increase that would occur after an infinite time of storage $(M-M_o)/(M_\infty-M_o)$. The M_∞ value was calculated by fitting the experimental weight-average molecular weight data at each temperature to the first-order reaction equation in the form representing conversion:

$$-\ln(1-\alpha) = k*t$$

Rate constants (k) were calculated assuming M_∞=950 and had the values of 0.0082 days^{-1} at 37°C, 0.223 days^{-1} at 60°C, and 2.733 days^{-1} at 90°C. The activation energy for the processes occurring during storage determined from these data was 102±11 kJ/mole, and the frequency factor (A) was exp(35.1).

Table 3. Apparent Weight-Average Molecular Weights of Stored Pyrolysis Oil

37° C		60° C		90° C	
Time days	M_w	Time days	M_w	Time hours	M_w
0	530	0	530	0	530
7	540	1	610	1	560
17	580	2	680	2	600
17	580	2	680	2	610
28	630	3	730	4.5	690
56	690	6.7	860	8	790
84	730	9	890	15	860
84	740	9	900	15	880

This model allows us to predict the values of the weight-average molecular weight of the oil as a function of the storage conditions. The predicted versus experimental values are presented in Figure 2. The deviations between measured and calculated values are in most cases less than 5%. Regarding the complexity of the reaction system, this correlation should be considered successful, even though the values at 60° C were consistently underestimated.

The molecular weight distribution of an oil strongly influences its viscosity, an important property to be considered in designing combustion equipment such as pumps and atomizers. Assuming that the viscosity changes with storage in the same way as the molecular weight of the oil, a limiting value of 376 cP (at 40° C) was calculated. The viscosity of the stored oil calculated using this value and the above-reported values for the activation energy E_a and the frequency factor A are shown in Figure 3. Although the agreement between measured and calculated values is not quite satisfactory in the high conversion region, the viscosity of the stored oil can serve as an approximate measure of the progress of aging processes. The applicability of the model is likely to be limited to this pyrolysis oil because the viscosity of oils strongly depends not only on the concentration of high-molecular-weight components, but also on their water content. A higher water concentration would also be expected to slow down condensation processes in the oils. The M_∞ value was obtained by finding the best fit of the data for this particular oil, and it is likely that other biomass oils will exhibit different limiting values of molecular weight. However, the proposed method could be useful to evaluate changes in other biomass oils.

3. Corrosiveness of Pyrolysis Oils

Biomass pyrolysis oils contain substantial amounts of organic acids, mostly acetic and formic acid, and for this reason are corrosive to certain common construction materials. Soltes and Lin [3] studied corrosion rates of metals by Tech-Air wood pyrolysis oil. They found that this oil was corrosive to steel and aluminum, and, surprisingly, to 304 stainless steel. It is interesting that the 304 S.S. was not

corroded by the acetic-formic acid solution of the same concentration as in the pyrolysis oil. The oil was not corrosive to stainless steel 316 nor to copper (corrosion rate less than 2 mils per year).

Aubin and Roy [4] found that factors other than acid concentration in the oils contribute significantly to the corrosion properties of the oils. Their study on vacuum pyrolysis oils indicated that increasing temperature and water content of the oil resulted in a dramatic increase in its corrosion activity. Although the oils proved to be highly corrosive to carbon steel throughout most of the range of the studied conditions, they were noncorrosive to both 304 and 316 stainless steels.

An important group of materials being considered for construction of pyrolysis oil storage tanks is polymers. Two of them - polyester resin and high-density polyethylene - were tested at NREL for chemical resistance to vortex reactor oak pyrolysis oil. The test was conducted according to ASTM method D 543-87. Duplicate samples (2 in. x 1 in.) were exposed to the oil at two temperatures, 20°C and 60°C, for 40 days. The materials submerged in the oil at 20°C did not visibly change, while those exposed at 60°C showed discoloration, that was more pronounced for polyethylene than for polyester. At 20°C, the weight increased by 0.22% for polyester samples and by 0.05% for polyethylene. At 60°C, the weight increase was 0.75% and 0.35% respectively. Both materials exposed to the oil at 60°C increased in thickness by 0.06 mm. The permissible thickness variation is 0.18 mm for hot molded materials and 0.30 mm for cold molded materials after 7 days of exposure.

4. Conclusions

1 Properties of biomass pyrolysis oils change during storage. Although the pH is not much affected, the water content, viscosity, and molecular weight of the oil increase with the time and temperature of storage.

2. The changes in molecular weight and the viscosity of the oil can be predicted as a function of storage conditions using first-order kinetics.

3. Pyrolysis oils are corrosive to steel and aluminum and are noncorrosive to stainless steel and polymers.

4. The oils should be stored in air-free stainless steel or plastic tanks at room temperature or refrigerated.

Acknowledgements

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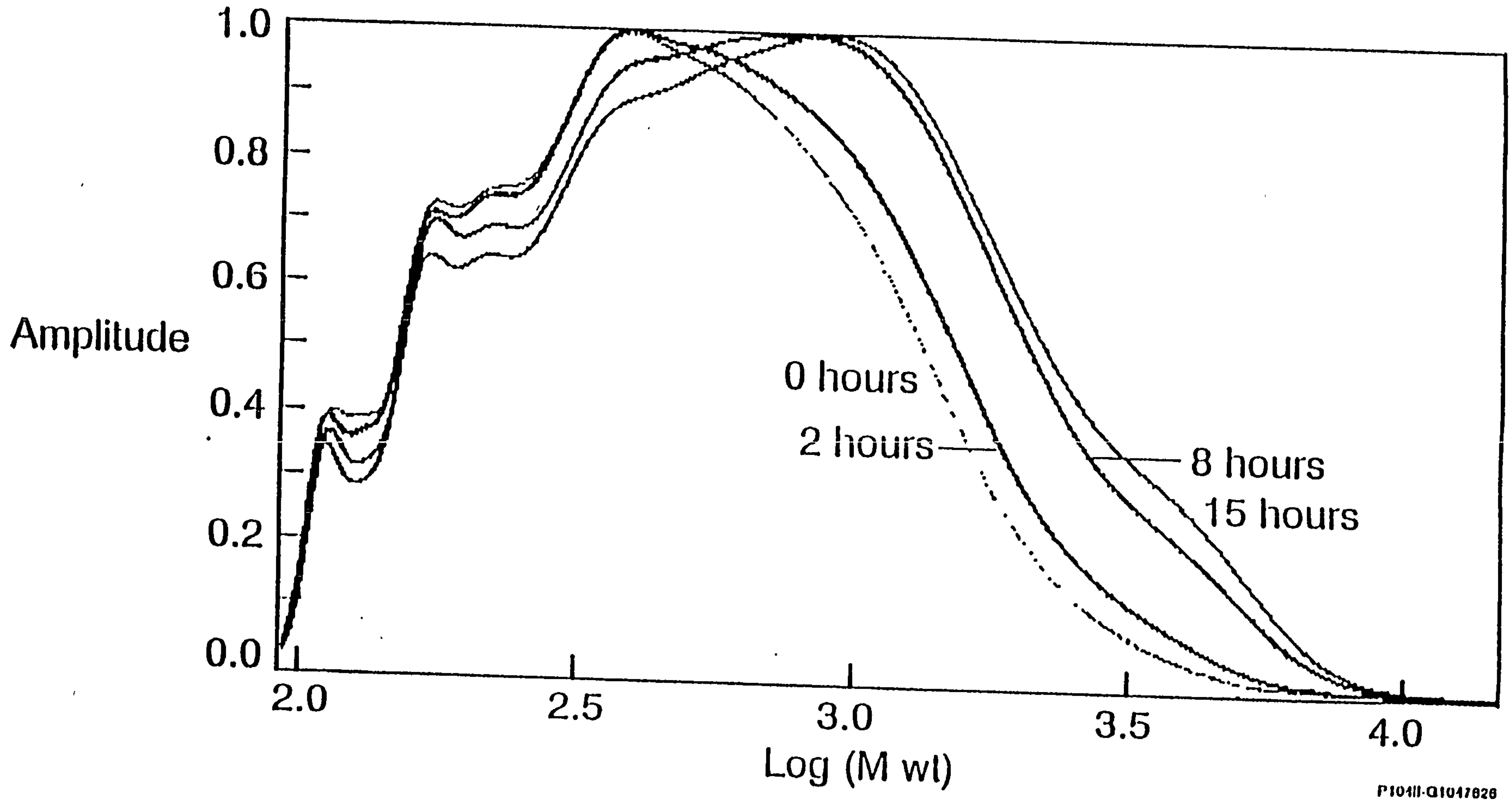


Figure 1. Molecular Weight Distribution of Pyrolysis Oil Stored at 90°C

Figure 2. Prediction of Weight-Average Molecular Weight of Stored Oil.
$M_\infty = 950$, $\ln A = 35$, $E_a = 102$ kJ/mol

■ 37°C, ◆ 60°C, ▲ 90°C

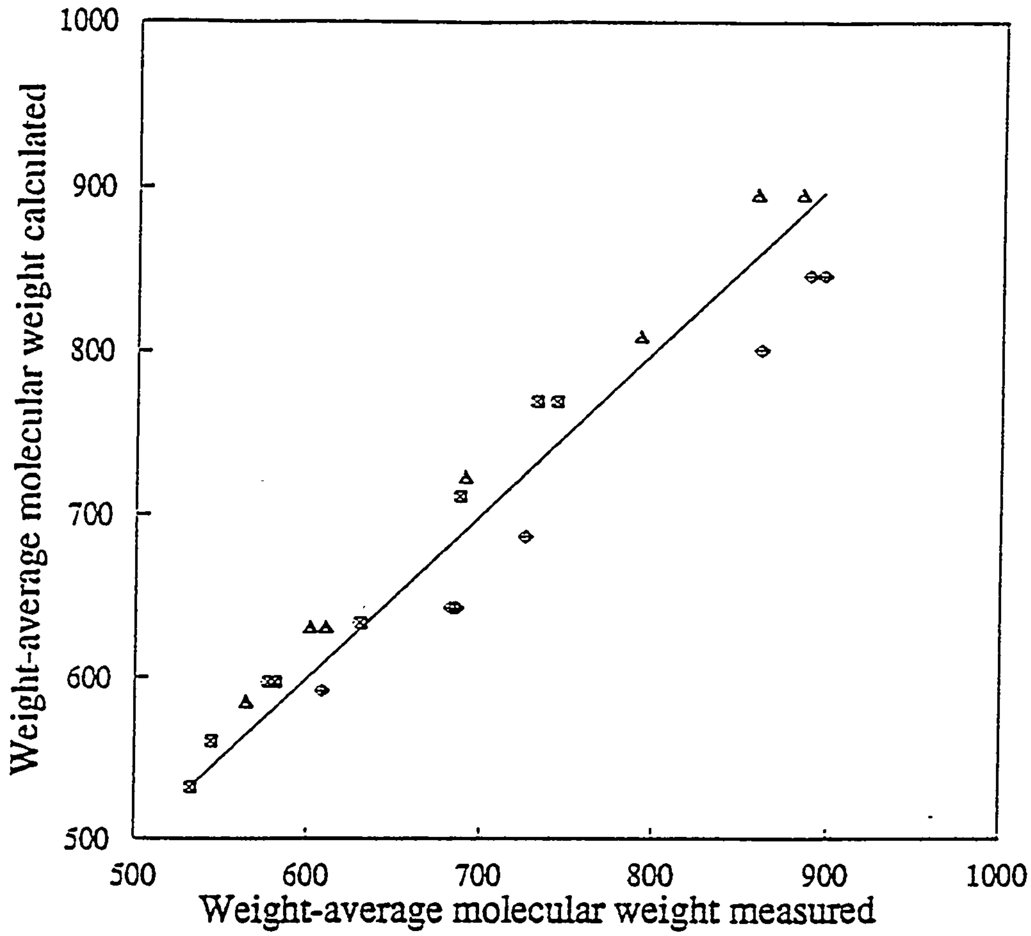
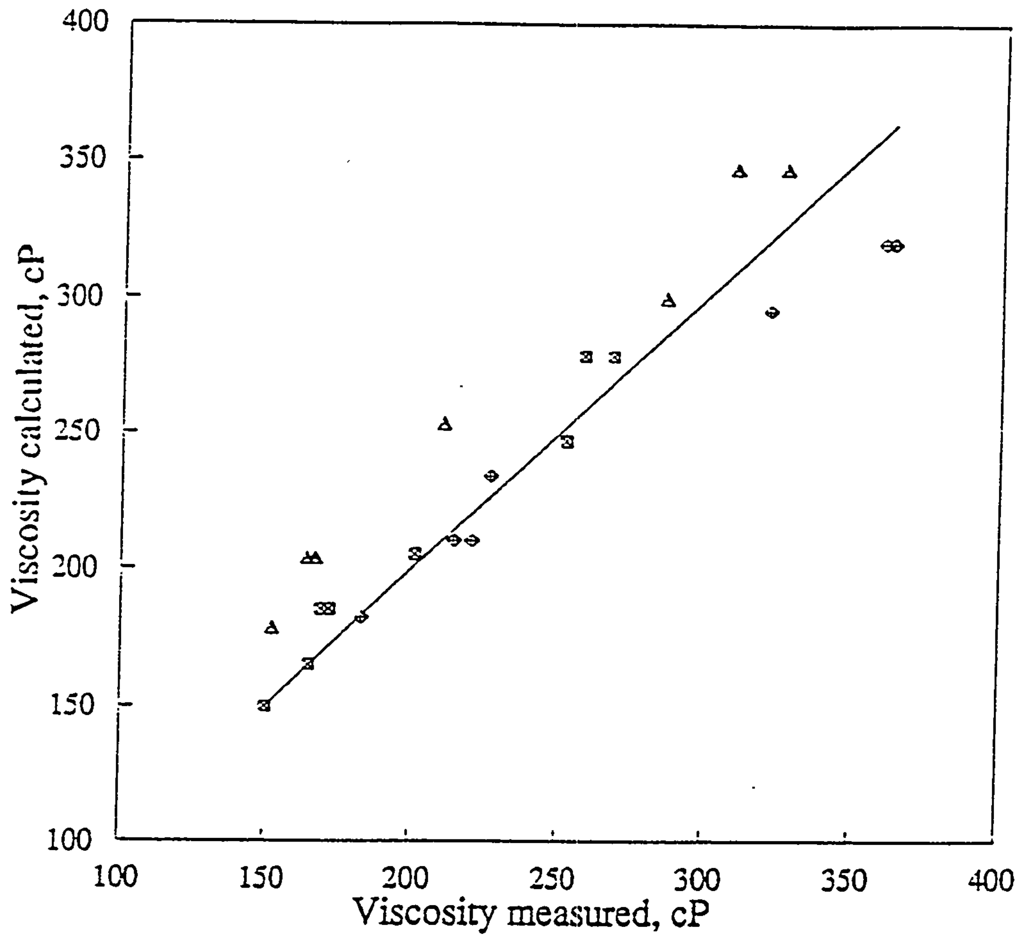


Figure 3. Prediction of Viscosity of Stored Pyrolysis Oil

■ 37°C, ◆ 60°C, ▲ 90°C



INORGANIC COMPOUNDS IN BIOMASS FEEDSTOCKS: THEIR ROLE IN CHAR FORMATION AND EFFECT ON THE QUALITY OF FAST PYROLYSIS OILS

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Abstract

Inorganic compounds especially potassium, calcium, sodium, silicon, phosphorus, and chlorine are the main constituents of the ash in biomass feedstocks. The concentrations of ash in biomass feedstocks range from less than 1% in softwoods to 15% in herbaceous biomass and agricultural residues. During biomass pyrolysis, these inorganics especially potassium and calcium, catalyze biomass decomposition and char formation reactions. Decomposition reactions may either result in levoglucosan-rich or hydroxyacetaldehyde-rich pyrolysis products depending on the concentration of the ash in the feedstocks. The catalytic effect of the ash levels off above 1.5% concentration. Chars formed during these reactions invariably end up in the pyrolysis oils. A high proportion of the alkali metals in the ash are sequestered in the chars and are suspended in the pyrolysis oils as submicron particles. These submicron char particles tend to agglomerate under cold storage conditions. The presence of high concentrations of alkali metals in the biomass pyrolysis oils makes them unsuitable for combustion in boilers and in turbine operations. The highest concentration of alkali metals are found in herbaceous feedstocks and agricultural residue pyrolysis oils.

Sequential cold filtration of the oils using filters of varying size revealed that most of the alkali metals detected in the pyrolysis oils are indeed trapped in the chars. Leaching studies conducted on the chars suspended in the oils showed no leaching of alkali metals from the chars into the oils. The alkali metals in the oil therefore originate from the suspended submicron char particulates. Our data suggest that hot gas filtration of the oils can effectively reduce the alkali metal contents of the pyrolysis oils to acceptable levels to be used as turbine and boiler fuels.

Introduction

The potential of biomass pyrolysis oils (biocrude) for large scale power production is attractive because of the hauling cost associated with the use of solid biomass, easier handling, distribution, and storage of liquid fuels. Additionally, biocrude is a potential feedstock for chemicals, it is highly oxygenated, and above all, it is a renewable resource. If biomass feedstock production is managed sustainably, the use of biocrude for power

generation will have no net contribution to the atmospheric carbon dioxide because the carbon dioxide produced during the combustion process would be captured by the plants during their growth. However, biocrude like any other fuel in their developmental stage, is plagued with several unique problems that have to be solved before it can have any significant impact on fuel supply. Some of the common problems associated with biocrude are: high acidity, high viscosity, instability during storage, high corrosiveness, high water content, alkali, and alkaline earth metal contents.

The alkali and alkaline earth metals content (especially potassium, sodium, and calcium) is the focus of this paper. The presence of these metals in biocrude have been projected as potential sources of fouling, corrosion, and erosion of turbine blades in power generation systems as well as fouling of steam boilers. This projection stems from the stringent specification of alkali metal contents in turbine fuels derived from petroleum resources. Because of the high sulfur contents of petroleum-derived turbine fuels, the presence of more than 1 ppm of alkali metals in these oils is unacceptable. It has been shown that the alkali metals form sulfates with sulfur oxides produced during combustion and these sulfates are principal sources of hot corrosion. Because the sulfur content of petroleum derived fuels cannot be reduced through distillation, there is a stringent requirement to lower the potassium and sodium contents of these fuels [1].

Gas turbine operators have shown that slag-forming compounds in oils can cause corrosion and deposit . Corrosion can result from vanadium, potassium, sodium and lead. These elements in addition to calcium can form deposits which are very difficult to remove from turbine blades [1]. Operation of biomass-fired turbines have also shown that, if gas inlet temperatures are less that 800°C, ash deposits on the turbine blades, which are extremely difficult to remove [2].

Pyrolysis oils produced from various biomass feedstocks which use fast pyrolysis processes are known to contain very high levels of alkali and calcium metal salts but those produced by vacuum pyrolysis have relatively low alkali and calcium contents [3]. However, the mechanism of inorganic material deposition in pyrolysis oils is not known. In this paper we discuss the probable mechanism of alkali metal deposition in the pyrolysis oils and in a companion paper to be presented at this workshop, some of the proposed methods of alkali metal removal are discussed [4].

Experimental

Pyrolysis Molecular Beam Mass Spectrometric Analysis (Py-MBMS).

Biomass feedstocks used in this study consisted of tall fescue (*Festuca arundinacea* Schreb.), alfalfa-orchardgrass (*Medicago sativa* L.-*Dactylis glomerata* L.), and switchgrass (*Panicum virgatum* L.) with different ash contents because of biological degradation. The biomass feedstocks were ground to 40 mesh and weighed in triplicates in quartz (20-

30 mg) and pyrolyzed at 500 °C in a hot helium atmosphere for 1.5 seconds. The pyrolysis was monitored by a molecular beam mass spectrometer (MBMS). The residue after the pyrolysis was cooled in helium gas at STP and weighed. The moisture content of the feedstock used for these studies was 5.6-6.2%.

Fluidized Bed Pyrolysis of Biomass Feedstocks.

To study the origin of alkali metals, calcium, and other trace inorganics content of biocrude, switchgrass (*Panicum virgatum* L.) was pyrolyzed in a fluidized bed reactor. Detailed description of the fluidized bed reactor has been published elsewhere [5]. The switchgrass samples were milled in a Wiley mill (model 4) to a Sauter mean diameter of 345-400 μm. The pyrolysis temperature of the fluidized sand bed was 500 °C and the fluidizing gas was nitrogen. The pyrolysis vapor residence time in the free volume of the reactor was <0.4 s. Pyrolysis vapors were condensed in a condensation train which consisted of chilled water condenser, ice/salt condenser, electrostatic precipitator, and a cotton wool trap. The oils from the condensers were recovered by washing with acetone. The acetone washed oils were made up to a total volume of 5 L and samples of 200 mL x 3 were taken from the unfiltered oil. The oils were then filtered sequentially through a 40-60 μm, 10-15 μm, 4.0-5.5 μm, 1.0 μm, and 0.7 μm filters. During each filtration stage, 200 mL x 3 samples were taken. The acetone soluble oils were recovered by rotary vacuum evaporation (18 mm Hg and 40 °C). The samples were sent to Huffman Laboratory, Golden, Colorado for ash, potassium, sodium, calcium, silicon, chlorine, and phosphorus analysis.

A second set of samples was prepared by filtering acetone soluble oils through a 40-60 μm filter and storing a 5 L sample in a cold room (10 °C) for 1, 2, 7, 15, and 30 days. At the end of each storage period, 200 x 3 mL samples were taken and filtered through a 10-15 μm filter. The oil was recovered by vacuum evaporation as above. These samples were also analyzed by the same laboratory for the same elements as above.

Results and Discussion

Pyrolysis Molecular Beam Mass Spectrometric (Py-MBMS) Analysis

The herbaceous feedstocks used in this study were switchgrass, tall fescue and alfalfa-orchardgrass. Ash contents of these feedstocks ranged from 4 - 12% which were very high compared to woody biomass feedstocks. Part of the high ash content can be attributed to unprotected outside storage of the feedstock for a 9 month period duration. This outside storage resulted in both partial microbial degradation and weathering of the feedstocks, hence the ash contents increased very significantly and a wide variation of ash contents were observed for various samples.

In Figure 1, the char yields on moisture-free ash-free basis are plotted against the

potassium and calcium contents of the feedstocks. The influence of calcium and potassium contents of the feedstocks on char formation appears to be non-linear. At low inorganic concentrations in the feedstock, the catalytic effect appears to be more vigorous than at higher concentrations as shown by the steeper slope of the curve. At high potassium and calcium concentrations, the yield of char levels off under our pyrolysis conditions.

The above data suggest that there are at least two mechanisms of char formation: one initiated by inorganic constituents of the biomass and the other by condensation reactions of the pyrolysis products.

The char data suggests that activity of the inorganic materials is dependent on the number of active sites available in the biomass and char formation reactions are initiated from these sites only. Once the active sites are saturated, it appears the excess potassium and calcium present do not take part in the reaction. DeGroot et al [6] reported increase in char formation when inorganic salts were added beyond the exchange capacity of cottonwood, but they did not go beyond 2% of inorganics and thus they did not observe the levelling off effects observed in our study. However, they reported that the incremental effects of char yield was less as the ash level increased, which agrees with our data. They speculated that the sites available for ion-exchange of inorganic species is dictated by the amount of hemicelluloses present in the biomass feedstock. It has also been observed that the catalytic effect of inorganic species on the conversion of cellulose to hydroxyacetaldehyde appears to be non-linear and drops off with increasing amounts of inorganic ions [7, 8]. This again shows that the catalytic activity of the inorganic ions are directed by the number of active sites available, probably the number of uronic acid sites which bind the inorganic compounds. The potassium and calcium catalytic activity also appears to be mass transfer limited, because the inorganics appear to be the center of reaction and char formed during the pyrolysis reaction covers the surface of the particles. As the reaction proceeds, char builds up on the surface of the catalyst particle and slows down the reaction until it eventually stops. Thus char particles formed by this process will have a high concentration of inorganics in the center of the particle. This is illustrated by the high concentration of the inorganic material in the chars obtained from the fluidized bed pyrolysis of switchgrass described in the next section. However, the exact mechanism of the char formation is not understood. We did not investigate the effect of other inorganic materials present in the biomass feedstocks on char formation reactions, so that the levelling off observed in these data could have been influenced by the presence of other inorganic compounds in the biomass.

The Role of Char in Biomass Pyrolysis Oils.

We have shown above that the inorganic constituents of biomass feedstocks play some role in the formation of char during pyrolytic reactions. In the fluidized bed pyrolysis process, some of the char formed during the pyrolysis process is suspended in the fluidization gas and transported out of the reactor. A cyclone separator installed in the pyrolysis train captures over 90% of the char carried over by the fluidization gas, but char

particles below 10 µm normally escape from the cyclone and condense with the oil.

Table 2 shows the reaction conditions and the material balances for the fluidized bed pyrolysis runs of switchgrass feedstock. Total liquid yields were relatively low compared to pyrolysis of woody feedstocks under similar conditions. The char content of the pyrolysis oil after filtration through 40-60 and 10-15 µm was 2-3%. Smaller filter sizes did not produce any significant amounts of char. The ash contents of the chars recovered from the pyrolysis oils ranged from 9-15% while ash contents of the filtered oils were very low (<0.05%) except for the unfiltered oil that had ash content of 0.45%. The ash content of the chars was more than double that for the feedstock (Table 1). The high ash content of the chars suggests that a large fraction of the inorganic species was sequestered in the char fraction. This observation was confirmed by the high concentrations of the potassium and other elements in the char and low concentration of these elements in the pyrolysis oil (Table 3 and 4).

Although the ash content of the pyrolysis oil was very low (<0.05 to 0.49%), the potassium and calcium levels were prohibitively high for application as turbine fuel. The concentration of potassium in these oils range from 160 - 300 ppm, and those for calcium ranged from 1-95 ppm whereas turbine fuel specification requires total alkali metals content of 1 ppm. Concentrations of other inorganic elements in the pyrolysis oils were equally high (Table 3).

Sequential filtration of the condensed pyrolysis oils dissolved in acetone revealed some interesting results. The raw unfiltered oil as expected had the highest potassium and calcium contents but the contents of these metals decreased gradually as the raw oil was filtered sequentially through different filter sizes. The concentration of potassium and calcium finally levelled off at around 4-5.5 µm (see Figure 2). This concentration trend was similar for silicon and phosphorus in the oils. For chlorine and sodium, the data was very scattered and no concrete conclusion could be drawn on the effect of filtration of the oil on element distribution in the oil.

The gradual decrease in the potassium and calcium contents of the oil with the decrease in the filter size clearly suggests that fine char particles in the oils were partly responsible for the high concentration of these elements in the oils. Furthermore, oils from vacuum pyrolysis process which do not use fluidizing gas or entrainment gas as in the ablative pyrolysis (vortex reactor) process have been shown to contain very low concentrations of both char and alkali metals [3]. However, because the potassium and calcium contents of the oil did not extrapolate to zero (Figure 2), this also suggests that some of the inorganic material may reside in the oil phase or that there are submicron char particles which escaped the smallest filter (0.7 µm). Alkali metals and other inorganics may get into the oil phase by the following mechanisms: leaching of inorganics from the char into the oil phase; vaporizing of the inorganics during the pyrolysis run and condensation with the oils or a combination of both. Our thermodynamic calculations show that the vaporization mechanism plays a minimal role in the transport of potassium, sodium, and

calcium into the oil phase. At 500 °C, most potassium, sodium, and calcium salts have very low vapor pressure and therefore are not likely to contribute significantly to the inorganics in the oil phase. Thus the only credible source of transportation of alkali into the oil phase is through leaching of the inorganics sequestered in the submicron char that escaped capture by the cyclone separator.

The biomass pyrolysis oils have very low pH (2-3) because of the formic and acetic acids as well as glyoxal and other acidic compounds in the oil. Under these acidic conditions, it is possible that the inorganics could leach into the oil. The rate of mass transfer will depend on the concentration of the inorganic species, the char particle size, and the porosity of the particle.

Leaching of inorganics of pyrolysis chars

To ascertain whether leaching is the sole mechanism of mass transport of inorganics (especially) potassium into the oil phase, oil leaching studies were carried out. The data (Figure 3) show that within the limits of experimental error, the potassium content of the oil decreases with storage time. This result was very surprising to us because it suggests that, even under the highly acidic oil environment, there was no leaching of potassium from the char into the oil phase under the cold room conditions. Instead, it appears that there was agglomeration of the submicron char particles in the oils. These agglomerated submicron particles were large enough to be removed during the filtration stage and this resulted in the decrease in the potassium content of the oil during storage. However, this phenomenon equilibrates within seven days of storage of the oil samples and no further decreases were observed after 30 days od cold room storage. Similar trends in the concentration of other inorganic elements in the char were observed. It should be pointed out that studies at other higher temperatures could indicate otherwise because leaching rates are generally higher at higher temperatures.

Thus, it appears that alkali metals exist in the pyrolysis oils as sequestered suspension of submicron char particulates which do not leach into the oil phase under cold storage conditions. If the char particles could be removed from the pyrolysis vapors before they condense with the oils, or if a nanofiltration technique could be applied to the oils, then the alkali metal contents could be reduced to perhaps acceptable levels for use as turbine fuel. Preliminary hot gas filtration studies have indicated that the alkali metal content of the pyrolysis oils could be reduced to below 10 ppm, but at the expense of cracking some of the pyrolysis oils because of longer residence time in the hot filter.

Trace Inorganic Analysis

The analysis of trace inorganics in biomass pyrolysis oils appears to be a challenging task. According the local commercial laboratories in Colorado, the ashing of the oils using ASTM methods appears to be the most suspect of all the procedures. A graphitic type of carbon appears to be formed during the ashing process and this makes the ashing very

difficult. Furthermore, the atomic absorption method is limited to 10 ppm detection limit with a precision of ±10%. The heterogeneity of the oils make microsampling very difficult. The plots in Figures 2 and 3 clearly illustrate this point. The largest error bars are shown for the oil samples with the largest char concentration (unfiltered oil), but as the oil is filtered, the samples become more homogeneous and hence the error bars on the potassium and calcium determinations decrease. In a detailed discussion of this topic, Diebold et. al. [4] have shown that neutron activation analysis may be a better method of analysis for these oils.

Table 1. Composition of switchgrass feedstock

Element	Composition
Carbon (%)	45.1
Hydrogen (%)	6.1
Oxygen (%)	42.8
Nitrogen (%)	0.56
Chlorine (%)	0.68
Ash (%)	4.92
Calcium (ppm)	2400
Potassium (ppm)	8500
Sodium (ppm)	31
Phosphorus (ppm)	850
MJ/kg	

Table 2. Product yields and material balance for the fluidized bed pyrolysis of switchgrass feedstock.

	Run#1	Run#2
Pyrolysis Temp (C)	500	500
Char Yield (%)	18.8	19.0
Total Liquid Yield (%)	60.2	63.1
Gas Yield (%)	13.6	12.6
Mass Closure (%)	92.6	94.7

Table 3. Trace inorganic analysis of switchgrass pyrolysis oils. (The errors are standard deviations on 3 determinations).

Filter size (μm)	K (ppm)	Na (ppm)	Ca (ppm)	Si (ppm)	P (ppm)	Cl (%)	Ash (%)
Unfiltered	319±55	8.0±1.4	95±23	8.0±1.8	52±13	0.16±0.01	0.45±0.16
40-60	273±3	8.1±0.5	11±0.7	7.7±0.5	5.9±0.4	0.22±0.06	0.15±0.05
10-15	212±9	10.2±0.7	1.1±0.2	1.6±0.1	0.5±0	0.16±0.04	<0.05
4-5.5	163±6	13.5±1.4	0.7±0.1	1.3±0.5	0.4±	0.14±0.04	<0.05
1.0	177±5	16.1±0.5	1.5±0.2	2.0±0.2	0.5±0	0.12±0.01	<0.05
0.7	175±10	16.6±1.8	2.2±0.7	1.4±0.3	0.6±0.1	0.16±0.03	<0.05

Table 4. Trace inorganic analysis of chars recovered from the pyrolysis of switchgrass feedstock.

Source of Char	K (ppm)	Na (ppm)	Ca (ppm)	P (ppm)	Cl (%)	Ash (%)
Run #1 40-60 μm filter	7700	225	5600	2700	1.02	9.5
Run #1 10-15 μm filter	8500	690	7100	3600	1.06	15.3
Run #1 Char pot	24000	155	7300	2700	na	na

Conclusions

Inorganic materials (especially potassium and calcium) in biomass feedstocks catalyze pyrolysis reactions and are sequestered in the char. The potassium and calcium catalytic activity appears to be mass transfer limited, because the inorganics appear to be the center of reaction and char formed during the pyrolysis reaction covers the surface of the particles. These inorganic particles which are covered with carbonaceous char are mostly responsible for the alkali metals in the oils. Their contribution to alkali metals in the oils is through suspension of the macro and submicron particles in the oils.

There appears to be no leaching of alkali metals from the char particles into the oil phase under cold storage conditions. Because of the submicron nature of the alkali metal-laden char particles, reduction of alkali metals in the oils cannot be easily accomplished through the filtration of the condensed oils. The best approach for the reduction of the alkali metals and other inorganics in the oils will be the removal of the char particles from the pyrolysis vapors by hot gas filtration or nanofiltration of the condensed oils.

Agglomeration of the alkali metal-laden submicron char particles in the oil takes place during cold room storage and this may cause problems for long term storage, transportation, and utilization of biomass pyrolysis oils.

The heterogeneity introduced into the oils by the submicron char particles also introduces significant errors in microanalysis of trace metals in the oils. There is a need for the development of improved methods of biomass oil analysis.

Acknowledgements

The authors acknowledge R. Bain, NREL Biomass Program Manager and US/DOE Biofuels Systems Division. for funding the project.

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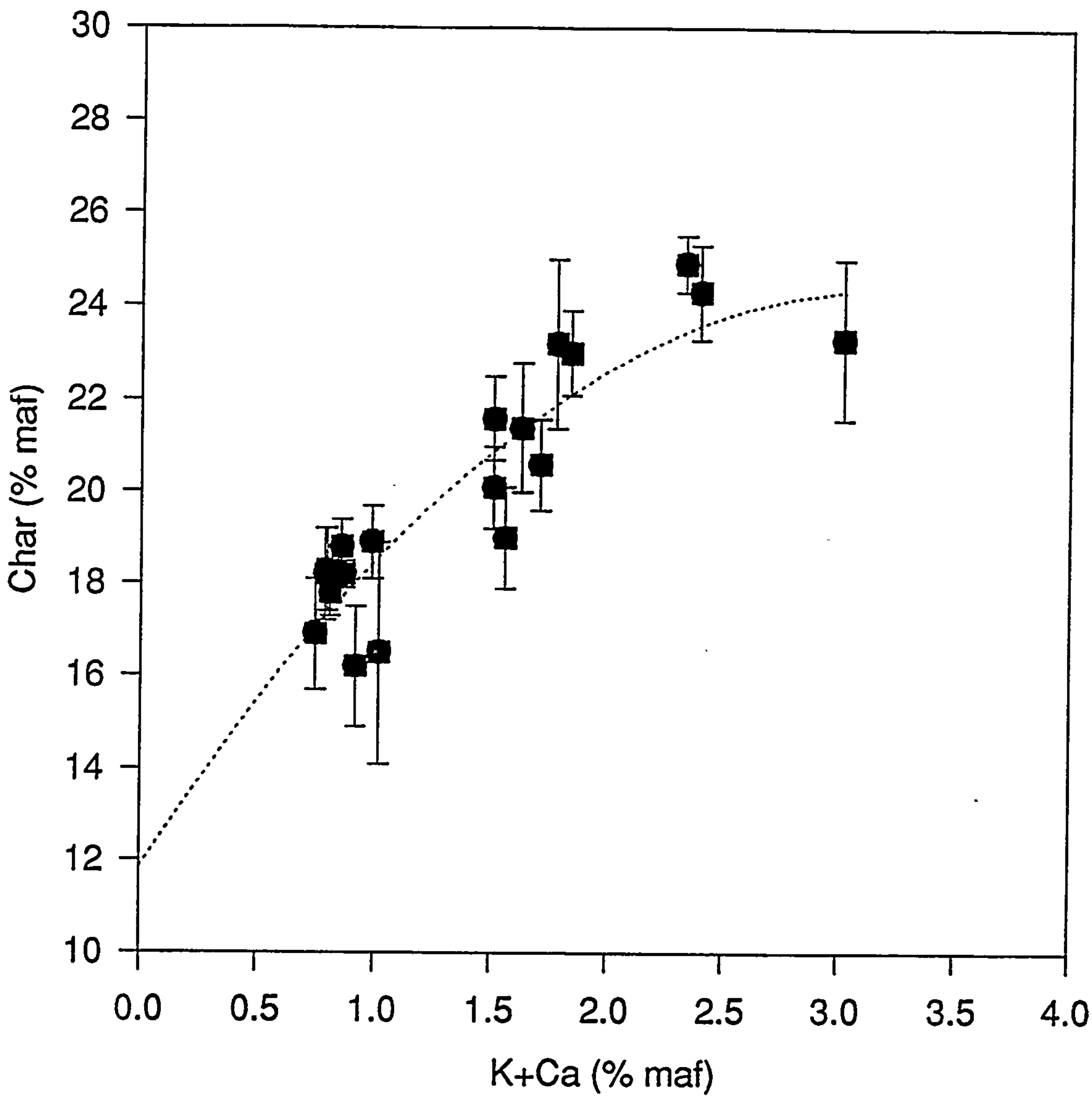

Figure 1. Influence of potassium and calcium contents of biomass feedstocks on formation at 600 °C.

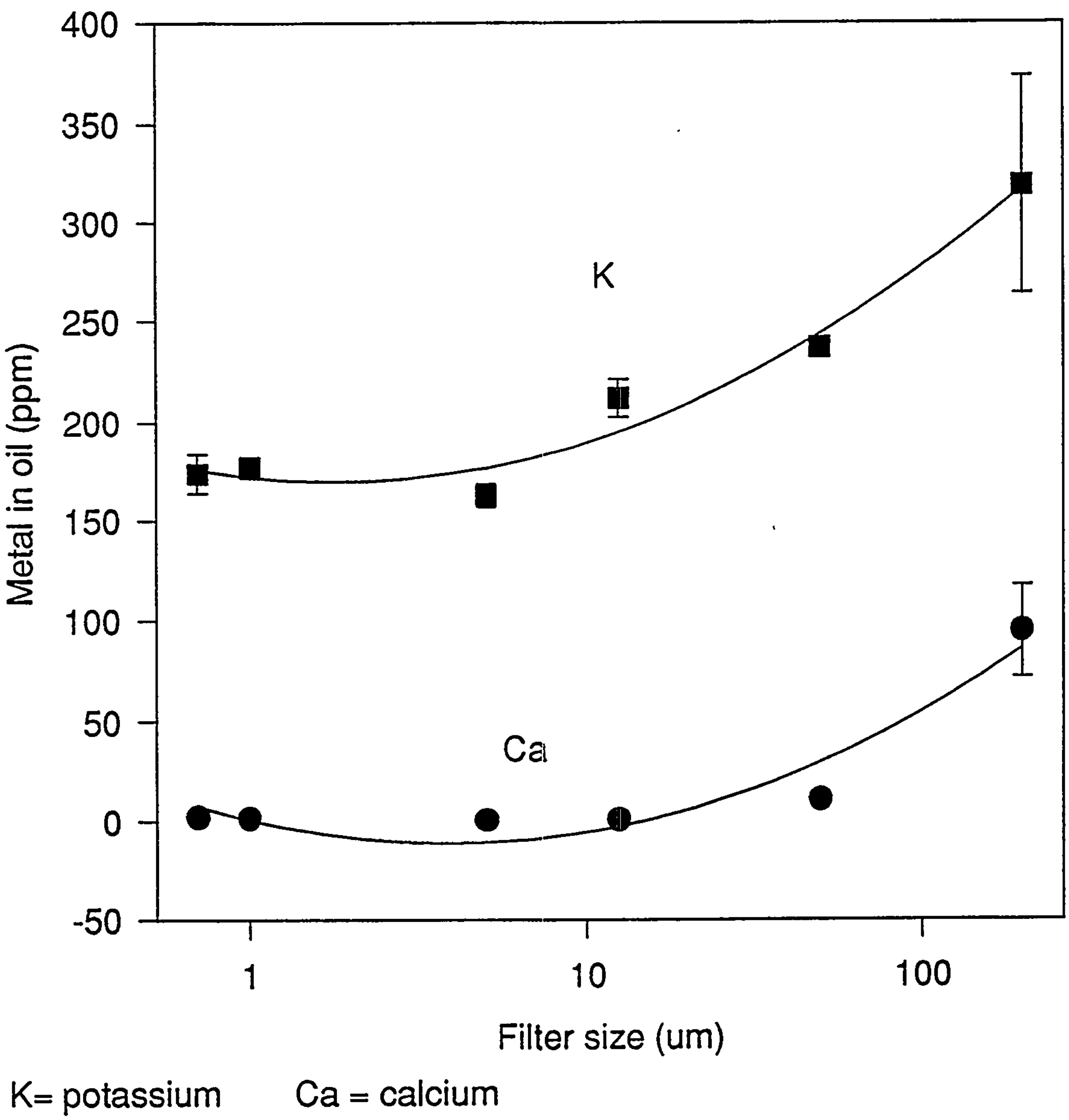

Figure 2. The effect of char on potassium and calcium contents of switchgrass pyrolysis oil. The oil was filtered through successive filters of decreasing pore size.

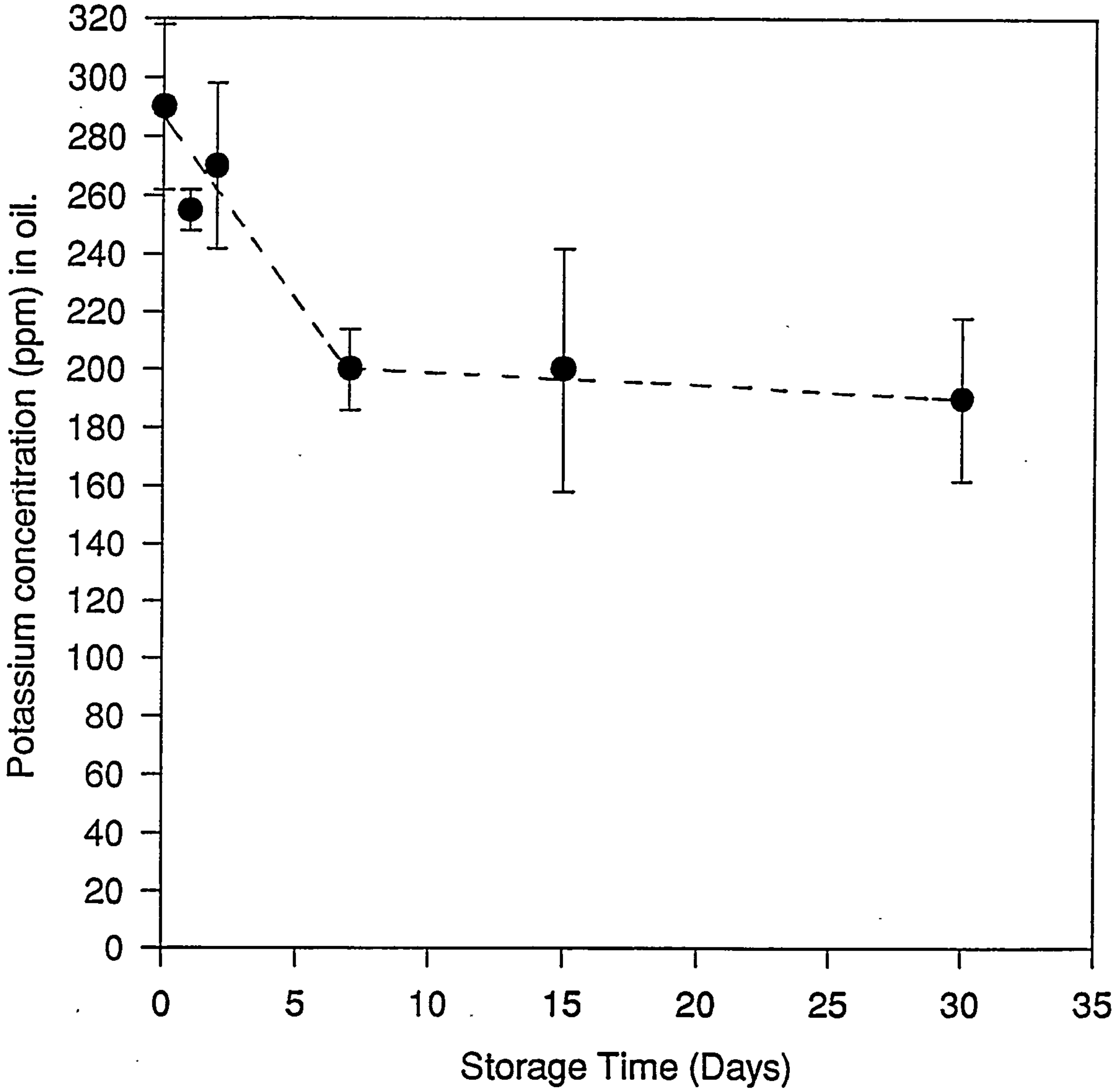

Figure 3. The influence of cold room storage on the potassium content of switchgrass pyrolysis oil. All oil samples were filtered through 10-15 µm filter before the potassium analysis.

HOT-GAS FILTRATION TO REMOVE CHAR FROM PYROLYSIS VAPORS PRODUCED IN THE VORTEX REACTOR AT NREL[1]

J.P. Diebold, S. Czernik, J.W. Scahill, S.D. Phillips, and C.J. Feik

ABSTRACT

The absence of char in pyrolysis condensates is required for them to be considered to have value above that of a residual fuel oil because of the alkali content of the char. During pyrolysis, the alkali-containing ash is concentrated in the char. This paper discusses hot-gas filtration of pyrolysis vapors produced in a vortex reactor at temperatures above the apparent dew point of the vapors prior to condensation.

A customized baghouse was commercially fabricated which has four filters and the ability to backflush each bag individually with a pulse of compressed gas. The size of the compressed gas pulse has been small enough to allow backflushing to occur during pyrolysis operations without shutting down. The nominal gaseous residence time of this design is on the order of three to five seconds. This baghouse is relatively unique in its capability to use either flexible, woven NEXTEL ceramic bags made by 3M or rigid sintered stainless steel filters made by MEMTEC. Based on samples of char made in the vortex reactor and collected with a cyclonic separator, the baghouse manufacturer projected a collection efficiency of 99.9%.

The cyclonic separator was removed from the vortex reactor system at NREL and replaced with the baghouse. A series of runs were made to evaluate this char separation technique to filter the total pyrolysis stream produced by the vortex reactor. The tendency of the pyrolysis oils to crack to permanent gases under these conditions is discussed as a function of operating temperature of the baghouse, based on previously determined kinetics.

Removing the char from the pyrolysis gas stream was demonstrated to be superior to that previously obtained using a cyclonic separator, based on the oil changing color from black to brown, lower ash content, and lower alkali metal content. In the case of switchgrass, the alkali metal content of the oil was lowered by two orders of magnitude. At the low alkali metal content of these oils, the analytical technique has not been very reproducible and has been under development. Heterogeneity of the oils has been blamed for the lack of reproducibility of the analysis for the several parts per million of alkali present.

BACKGROUND ON CHAR REMOVAL FROM PYROLYSIS OIL

Three products are formed during the pyrolysis of organic material: solid residue or char; permanent gases; and condensible vapors (organics and steam). Depending on the design of the pyrolysis reactor, the char is typically much smaller in size than the feedstock. With the vortex reactor, the char produced is a free-flowing powder. The mineral matter in the feedstock becomes concentrated in the char, giving the potential for mineral-free gases and condensible vapors if the char can be completely separated from the other products. In producing pyrolytic liquids from biomass and solid waste materials (e.g., short rotation woody crops, herbaceous crops, waste wood, municipal solid waste, etc.), a primary goal is to have a product that contains a minimum amount of suspended solids.

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[1]This paper was presented at the Specialists' Workshop on Biomass Oil Properties and Combustion, Estes Park, CO, Sept. 26-28, 1994.

Although the solid char has a high heating value per unit weight (about 50% more than the oxygenated, organic liquids), char in the oil severely lowers its value for the following reasons:

a) The solid char tends to settle slowly over time, leading to a sludge in the bottom of the storage vessel.

b) The solid char is very fine and increases the apparent viscosity of the oils, which can lead to the fouling of condensers in the production of the oil, as well as to problems in its utilization.

c) The solid char could plug the orifices of some burners and lead to difficulties in atomization and smooth combustion.

d) The burning characteristics of the solid char are different than those of the oil.

e) The char has a high ash and alkali metal content (about 7 times higher than the feedstock), which could damage boilers and turbines, as well as require flue gas cleanup equipment.

f) For turbine applications requiring less than 1 ppm alkali in the fuel, the high calcium, sodium, and potassium content of the char from biomass precludes use of pyrolysis oil with more than 0.02 weight percent char if made from wood or 0.002 weight per cent if made from switchgrass.

The value of the pyrolysis oil as a #6 fuel oil substitute for boiler use is relatively low at about $2.37/GJ ($2.50/MMBTU), compared to a premium gas turbine fuel value of about $4.27/GJ ($4.50/MMBTU). The removal of residual amounts of char from the pyrolysis oil could allow the oil to be substituted for the higher valued use in some applications. This is a very significant incentive to produce a pyrolysis oil with a very low char content. For catalytic upgrading of the pyrolysis oil vapors, the alkali content of the char fines would be expected to poison many of the catalysts now under consideration, i.e., ZSM-5 zeolites (Campbell 1983) (Beyerlein, et al 1993). The successful removal of char fines will set a standard for the cleanliness and quality of pyrolysis oil that will open new markets for the oil now under development in several DOE programs, i.e. Biomass Power, Biofuels, and Industrial Technologies.

The traditional method of removing solids from gas and vapor streams has been to use a cyclone separator. In the cyclone, centrifugal force created by the swirling action separates the dense solids from the low-density gases. The amount of centrifugal force generated is proportional to the square of the tangential entering velocity of the gas and solid mixture, as well as the inverse of the diameter of the cyclone. Higher efficiency cyclones have higher gas velocities, but also higher pressure drops and erosion. The efficiency of separation of the solids from the gas is a function of the diameter of the solids, with the smaller particles being more difficult to separate and collect. Thus, it is well known that the ability of a cyclone to remove solids from gases with a cyclone separator decreases as the cyclone is scaled up in size and as the particle size decreases, especially below 10 μm (Perry and Chilton 1973).

When NREL researchers produced pyrolysis oil at NREL using two cyclone separators in series, the size of the char particles in the oil was small enough to pass through a 10-μm oil filter, but large enough to quickly plug a 2-μm oil filter. The use of filters to remove char from the condensed

pyrolysis oil results in the formation of a sludge composed of char and oil. Disposal of this sludge in an environmentally acceptable manner will pose some difficulties. Because of its high viscosity and solids content, it would be difficult to pump the sludge into a furnace for incineration or back into the process for recycling. Due to the odor and water solubility of the pyrolysis oils, the sludge will not be welcomed in a landfill and would probably be considered a hazardous waste. In addition, because of the acidic nature of the oils, the alkali may be leached from the char before liquid filtration could take place to remove the char fines.

The ideal method of separating the char from the gases and vapors appears to be hot-gas filtration. In this approach, the solids are filtered from the hot vapors and gases prior to condensation. This results in the char fines being collected with the larger char particles and they become one char product that is a free-flowing powder. The formation of undesirable char/oil sludges is avoided. In addition, the proper action of the hot-gas filter is relatively easy to monitor with the pressure differential measured across the filter. In comparison, a malfunctioning cyclone separator can pass a large fraction of the char with very little change in the pressure drop across the cyclone. The primary scaling factor involved with a hot gas filter is the ratio of volumetric gas flow to the area of the filter, also referred to as the "face" velocity. A scaled-up filter merely has more surface area. The char collection efficiency of a filter is not expected to degrade as the filter is scaled up.
Gas filtering is typically done commercially in a baghouse filter. With this equipment, the solids are collected on the outside of cylindrical filter elements to form a filter cake. The filter cake is an important part of the filtering mechanism, as it will filter out progressively finer solids. The gases pass through the filtering media and are collected in a manifold leading to the clean gas outlet. A typical commercial-size baghouse might contain 50 to 200 filter elements. The baghouse is usually operated continuously with some means for automatic removal of solids from the filter. This allows the operators to maintain the pressure drop across the filter within a narrow range of values. For the purpose of efficient filtration, the operator will keep a higher pressure drop (a thicker filter cake) through the filter. In some cases, the solids can be removed by vibrating the filter elements. A more common method is backflushing; a fraction of the elements (e.g. one-fourth) will be periodically subjected to a pulse of reversed gas flow through the filter, which dislodges the collected solids and allows them to fall off the filters. The solids are gravity collected in a drum or a conveyer moves the solids to a holding tank. A common method of achieving this local back flow of gases is to pulse a jet of gas through an eductor mounted at the gas outlet of each bag or cylindrical filter element. The duration of the gas pulse is usually less than one second. This pulse of gas entrains the process gases with the motive gas and forces a reverse flow of gas back through the filter to expand and break the filter cake. Frangible pieces of the filter cake then fall to the bottom of the baghouse, where they can be removed.

The temperature of the pyrolysis stream during hot-gas filtration must be high enough to keep the pyrolysis oil in the vapor phase. If the oil were to condense on the filter, it would rapidly plug the filter. If the oil were to condense on the filter cake, the cake would become glued together (sintered) and difficult to remove in a continuous process. The temperature required to avoid oil condensation on the filter is currently under investigation at NREL, but appears to be around 350-400°C (660-750°F) based on previous experience. Any inert or carrier gases present in the vapor stream will serve to lower the effective dew point of the pyrolysis oil vapors. The high temperature required for hot-gas filtration eliminates many common fabrics for use as the filter bag material (e.g. cotton, nylon, polypropylene, Teflon, etc.). Another important consideration in the selection of filter media is the possibility of air leaking into the pyrolysis system and oxidizing the char on the filter; the filter should have to have the ability to withstand considerably higher temperatures than the nominal operating conditions.

Hot-gas filtration of a slipstream of pyrolysis vapors made from pine sawdust with the vortex reactor has been reported at 400°C with sintered Inconel filters rated at 2 and 5 μm (Diebold and Scahill 1988) (Scahill, et al. 1988). This system appeared to prevent char fines from reaching a fixed-bed of zeolite catalyst used to upgrade the vapors to hydrocarbons. Unreported operation at NREL was at temperatures as low as 365°C for short periods. The weight ratio of steam carrier gas to dry sawdust was between 1 and 1.5.

It has also been reported by the Technical Research Centre of Finland (VTT) that hot-gas filtering of fast pyrolysis vapors made from peat and pine bark with a fluidized bed pyrolysis system has been successfully performed at 350°C with weight ratios nitrogen carrier gas to dyr feed of 4 to 13. A small, but unquantified, amount of char was still observed in the condensates (Arpiainen and Lappi 1989). The filter was a commercial filter made of quartz fibers with a manufacturer's rating of 0.3 μm (Arpiainen 1994). Both the VTT and early NREL experiments passed the pyrolysis vapors through a cyclone separator prior to the filtering of the hot vapors. Neither of these two experiments were instrumented to observe the pressure drop across the filters, nor were these filters backflushed during the pyrolysis operation.

It is imperative that hot gas filtration of pyrolysis vapors be done at the lowest possible temperature for the following reasons:

a) At lower temperatures, the filter area can be smaller due to the contraction of the gas volume with temperature.

b) But more importantly, the pyrolysis oil vapors are not chemically stable at elevated temperatures and they will react to form permanent gases and a small amount of undesirable phenolics, which will further react to form polycyclic aromatic hydrocarbon (PAH) tars at elevated temperatures. The PAH tars are known to be carcinogenic in nature, whereas the initially formed pyrolysis oils apparently are not (Elliott 1988).

c) The decomposition rate increases exponentially with temperature, in a manner consistent with many chemical reactions (Diebold 1985).

Thus, the operator of a hot-gas filter to remove char from pyrolysis vapors must choose a temperature that is both hot enough to avoid condensation of the vapors and cool enough to minimize the conversion of oil to gases to an acceptably low value. Assuming that the process heat will be generated in large part by burning the permanent gases formed, some loss of the oil vapors will be acceptable. However, the quality of the oil begins to noticeably degrade if the gas produced exceeds about 20 wt% (Czernik, et al. 1993).

When the system is scaled up, the residence time of the pyrolysis vapors in the baghouse will need to be minimized by designing the system using the best estimates of the operating conditions. The usual practice of adding additional filter area (and consequently adding baghouse volume) for contingencies must be minimized. This will reduce the flexibility of the overall system, but is necessary to avoid unnecessarily long residence times in the baghouse. For a given temperature of operation, the loss in vapors will be directly proportional to the gaseous residence time.

EXPERIMENTAL EQUIPMENT

NREL has been investigating two very different filter media: a rigid sintered Inconel filter made by MEMTEC and a flexible ceramic cloth filter made of Nextel by 3-M. These filter materials have been extensively tested at temperatures considerably higher than would be used for the production of pyrolysis oil, but typical of the oxidative environment found in catalyst regeneration and flue gas applications (Parkinson 1989) (Lit and Conkle 1991).

At NREL, a baghouse that was custom made by Fisher-Klosterman has been used to develop hot-gas filtering of pyrolysis products. The design of this baghouse was based on design iterations between Fisher-Klosterman and J. Diebold at NREL, which resulted in a ten-fold reduction in the volume of the baghouse and the unique ability of the baghouse to be fitted with either the sintered Inconel or the 3-M Nextel filters. The final design of the baghouse minimized the internal volume, while retaining sufficient space between the filters and the walls to permit dirty gas flow and the filter cake to accumulate and be removed. It has four filter elements, each of which is separately backflushed with a supersonic burst of nitrogen or other pressurized gas through an eductor. This creates a backward flow of process and motive gas through the filter element. The char then falls into a receiving drum. The outside of the baghouse is heated with electrical heating tapes to maintain the walls at a desired temperature.

This small baghouse was designed for a gas-flow rate of 1.7 m^3 (60 ACFM) and has 1.0 m^2 (11 ft^2) of filter surface. The baghouse is constructed of stainless steel to withstand the high temperatures possible in the system. The body of the baghouse is a 12-in. (30 cm) pipe with a conical solids outlet in the bottom. Access to the baghouse is through a 12-in. (30 cm) top flange, which also holds the bag manifold plate sandwiched in place. When the top flange is removed, the manifold plate can be removed through the top. Suitable high-temperature gaskets are employed. The filters are held by the bag manifold plate. The nominal residence time of the gases and vapors in the baghouse is about 3-6 seconds at typical operating conditions.

The performance of this baghouse was predicted by the manufacturer based on a sample of wood char recovered from the NREL vortex pyrolysis reactor with cyclonic separators. The particle size analysis of the char showed 56 wt% less than 3 μm, 95% less than 9 μm and 99.09% less than 18 μm, as determined by liquid sedimentation. The filter was predicted to collect 99.9% of the char. This corresponds to a predicted char content in the oil of 0.02 wt%. Based on the requirement of less than 1 ppm alkali in turbine fuel, the vendor's predicted performance of the baghouse will need to be achieved for wood feedstocks low in alkali and exceeded for herbaceous feedstocks high in alkali.

EXPERIMENTATION

NREL has operated the char baghouse in 17 separate experiments. Some of the highlights of our experiences are described below.

Run 155 with sintered Inconel filters

Run 155 was the first time we used the baghouse to provide biocrude oil for the Biomass Power Program. Major changes to the pyrolysis system were made prior to this run, including installation of a new hopper and a new pyrolysis furnace. In this run, oven-dry switchgrass was fed into 20 kg/h of nitrogen-carrier gas at a nominal rate of 14 kg/h. The five sections of the vapor cracker transfer tube were set at 450° C. The baghouse was located between the vapor cracker transfer tube and the cyclone condenser. We used sintered Inconel made by MEMTEC as filters. The char cyclones had been removed from the system at the recommendation of the baghouse manufacturer. The

temperature near the top of the filter increased from 437° C to 470° C during the first 48 minutes of the run, then remained between 472° C and 476° C for the remaining 45 minutes of the run. These high temperatures contributed to low biocrude oil yields, but the filters did not plug with condensed oils.

The first attempt to backflush the sintered MEMTEC filters occurred 16 minutes into the run using motive nitrogen at 210 kPa gauge (30 psig) for a 0.05 second burst. This was ineffective, so the pulse duration was increased to 0.1 second. This was also ineffective. The pressure was then increased to 365 kPa gauge (53 psig) with the same pulse duration. Although the first pulse at these more severe settings was not successful, the second pulse reduced the pressure drop from 2500 to 2000 Pa (10 to 8 in. W.C.) The third pulse reduced the pressure drop to 1500 Pa (6 in. W.C.). As shown in Figure 1, this resulted in the desired drop in the pressure across the filter. These backflushing pulses were periodically used one at a time to keep the pressure drop below 2500 Pa (10 in. W.C.) until 49 minutes into the run. At this time, a series of 8 pulses (2 per filter candle) were delivered when the feed had been momentarily turned off, but with the carrier gas still on. This temporarily reduced the pressure drop to 375 Pa (1.5 in. W.C.) before the feeding was resumed. The pressure was then increased to 455 kPa gauge (66 psig) and the pulse interval reduced to 0.075 seconds. The run then proceeded with an occasional backflush that resulted in a temporary reduction of the pressure drop. At 70 minutes into the run, the duration of the pulse was increased to 0.10 seconds, which resulted in better pressure recoveries. At about 80 minutes into the run, feeding problems developed as indicated by the leveling of the pressure drop across the filter. All four bags were backflushed while the feeding system was cleaned out. At 92 minutes into the run, the pulse duration was set back to 0.075 seconds. The reduced pulse duration was not as effective in the removal of the char cake and the pressure drop increased. Repeated backflushing brought the pressure drop back down to the 2000 Pa (8 in. W.C.) region before the run was stopped. All bags were backflushed twice with 455 kPa gauge (66 psig) nitrogen for 0.075-second pulse durations after the feed had stopped.
Post-run examination of the filters revealed that a permanent char cake about 3-mm thick had remained on the rigid filter elements. The cake was frangible and easily vacuumed from the filter using a dusting brush. The recovered char had fallen freely into the char drum attached to the bottom of the baghouse, with no evidence of bridging or other problems. The char in the drum was very fine with a black talcum powder appearance. There was a very thin deposit of char fines downstream of the filter, just enough to fail a white glove inspection. The baghouse had a faint phenol or Lysol odor. We concluded after this run that the higher nitrogen pressures gave better backflushing.

RUN 157 with sintered Inconel filters

The primary purpose of this third run with the baghouse was to provide biocrude oil for the Biomass Power Program. Dry switchgrass was fed at 17.5 kg/h for the first hour and then at 15.4 kg/h for most of the rest of the run. The nitrogen-carrier gas flow was 20 kg/h. The baghouse filter was the rigid, sintered metal filter. The temperature of the vapor cracker (transfer line) was set at 400° C, but was always above the set temperature at between 475° at the inlet to 425° C at the outlet. The temperature of the upper portion of the bag was between 400 ± 5° C during the run, except for a brief drop to 384° C that occurred at 138 minutes into the run, immediately after the feeding had been interrupted for 22 minutes and then restarted. Based on the dry switchgrass fed, the yields were 38 wt% dry organic oil, 16% water, 22% char, and 20% gas. The mass closure was 95%.

The pressure drop created by the baghouse filters during this run is shown as a function of feeding time in Figure 2. This figure shows the maximum pressure curve just before the backflush operation and the minimum pressure curve immediately after the backflush. Backflushing occurred for every

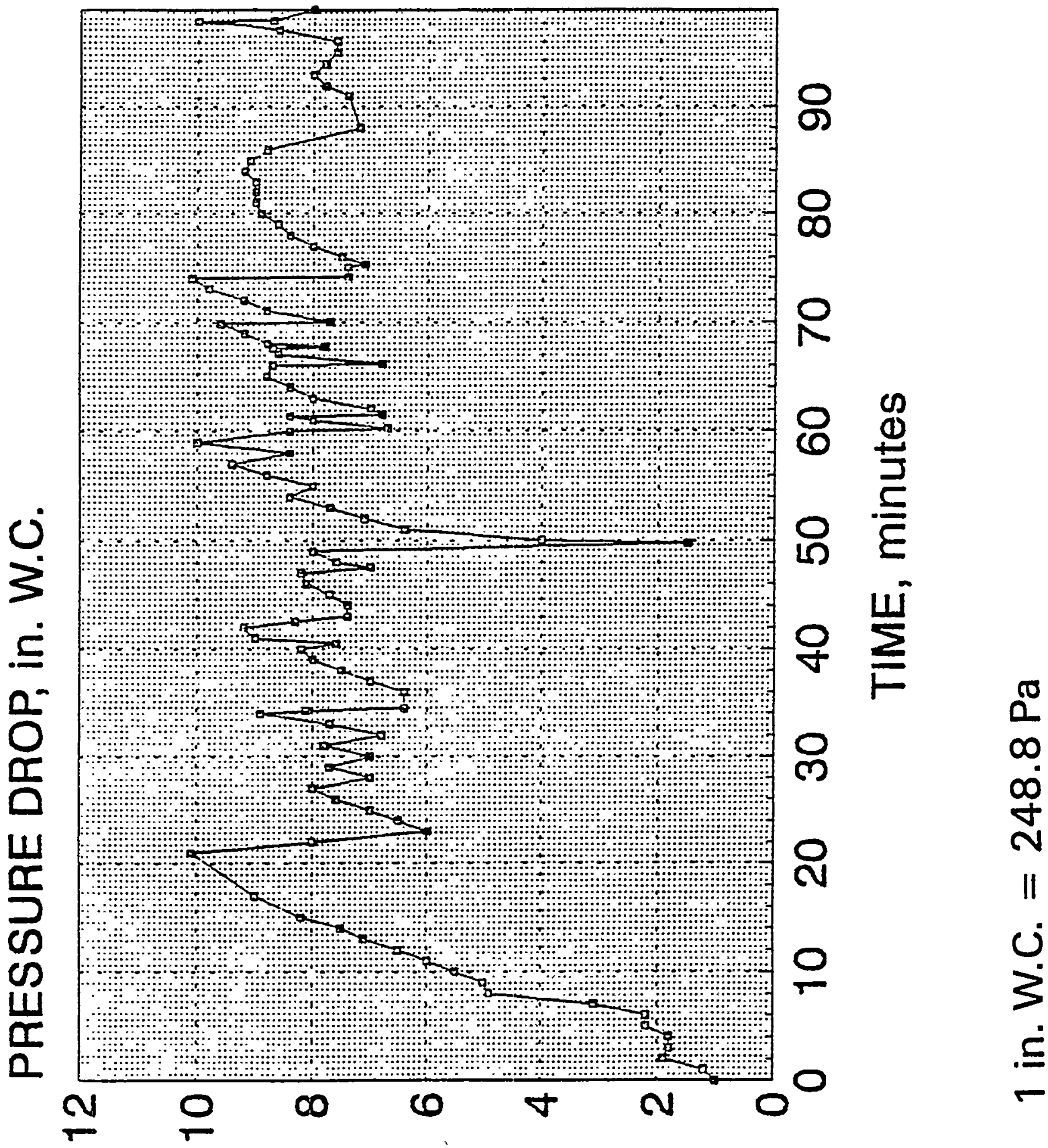

Figure 1. Baghouse Performance. Run 155--Switchgrass with Inconel filter.

data point on the minimum pressure curve. The pressure drop recovery is the difference between the two curves.

Based on the results of Run 156 (not discussed herein), where backflushing did not seem effective when high pressure drops existed across the filter, we decided to initially try to keep the pressure drop very low across the filter. Consequently, the first backflush occurred early in the run after 5 minutes of operation using 350 kPa gauge (50 psig) nitrogen for a 0.1-second pulse. The feed was turned off momentarily at 17, 33, and 52 minutes into the run feeding time. The large pressure drop recovery seen at 33 minutes was the result of backflushing all four filters. It soon became apparent that frequent backflushing would not keep the pressure drop as low as had been hoped, apparently due to the buildup of a permanent cake on the filter that was not being removed during the backflush. The backflush motive gas pressure was increased to 520 kPa gauge (75 psig) at 50 minutes into the feeding time with no apparent improvement in the pressure drop recovery. The motive pressure was increased to the maximum available of 650 kPa gauge (95 psig) at 56 minutes and the pulse duration was increased from 0.1 to 0.15 seconds. The pulse duration was incrementally increased again to 0.2, 0.3, 0.4, and finally to 0.5 seconds at 76 minutes into the run. (The maximum pulse duration setting of the backflush controller is 0.5 s.) The pressure drop recovery after each pulse was still relatively small. After 88 minutes of feeding, each backflush entailed all four of the filters receiving a pulse. This finally showed a good pressure drop recovery of several hundred Pascals (inches W.C.). The pressure drop seemed to reach an operating plateau of between 3200 and 3900 Pa (13 and 15.5 in. W.C.). After the feed was shut off at a feeding time of 138 minutes and then restarted, the pressure drop increased to a higher plateau of 4200 to 5000 Pa (17 to 20 in. W.C.). However, the long-term trend during the run was toward a progressively higher pressure drop across the filter. At the end of the run, the pressure drop was 5200 Pa (21 in. W.C.). A total of 49 kg of switchgrass was fed.

Post-run inspection of the filters showed a permanent cake left on the filter about 5-mm thick. There were a few remnants of a thicker temporary cake about 5-mm thicker. It appeared that the permanent cake left on the filters did not blow off and redeposit. If the permanent cake had redeposited, it would have blanketed over the remnants of the temporary cake. However, the edges of the residual cake were sharply defined and did not have the appearance of a redeposit of the permanent or temporary cake.

RUN 160 with flexible ceramic filters

Run 160 was performed primarily to generate condensates for the Biomass Power Program. Poplar wood was fed at rates of 13 to 15 kg/h. Preheated nitrogen was used as the carrier gas at 20.6 kg/h. Temperature control of the baghouse was not as good as on previous runs. The filter bag temperature near the top of the baghouse was around 460° C at the beginning of the run, but decreased to 445° C by the end of the first 1.5 hours of the run. During the next 1.5 hours, the bag temperatures were between 431 and 442° C. The bag temperatures were around 400° C for the next hour, then during the last 30 minutes they started to drop to end at 331° C. The rapid variability of the bag temperatures is not characteristic, and the thermocouple may have been reading the exposed transfer line instead of the bag temperature. Inadvertently, no baghouse operating data were taken. A total of 59 kg of poplar wood was fed in this run. The yields based on the dry poplar fed were 36 wt% dry organic oil, 16% water, 12% char, and 24% gas, for a mass closure of 88%.

Post-run examination of the char filters showed a fine-grained, partially sintered, permanent cake on the filters. Over the permanent cake was a temporary cake, which was not obviously sintered. This indicates that for a short period of time in the run, there was some condensation of the biocrude vapors on the permanent filter cake. A possible scenario would be the following: when the system is shut

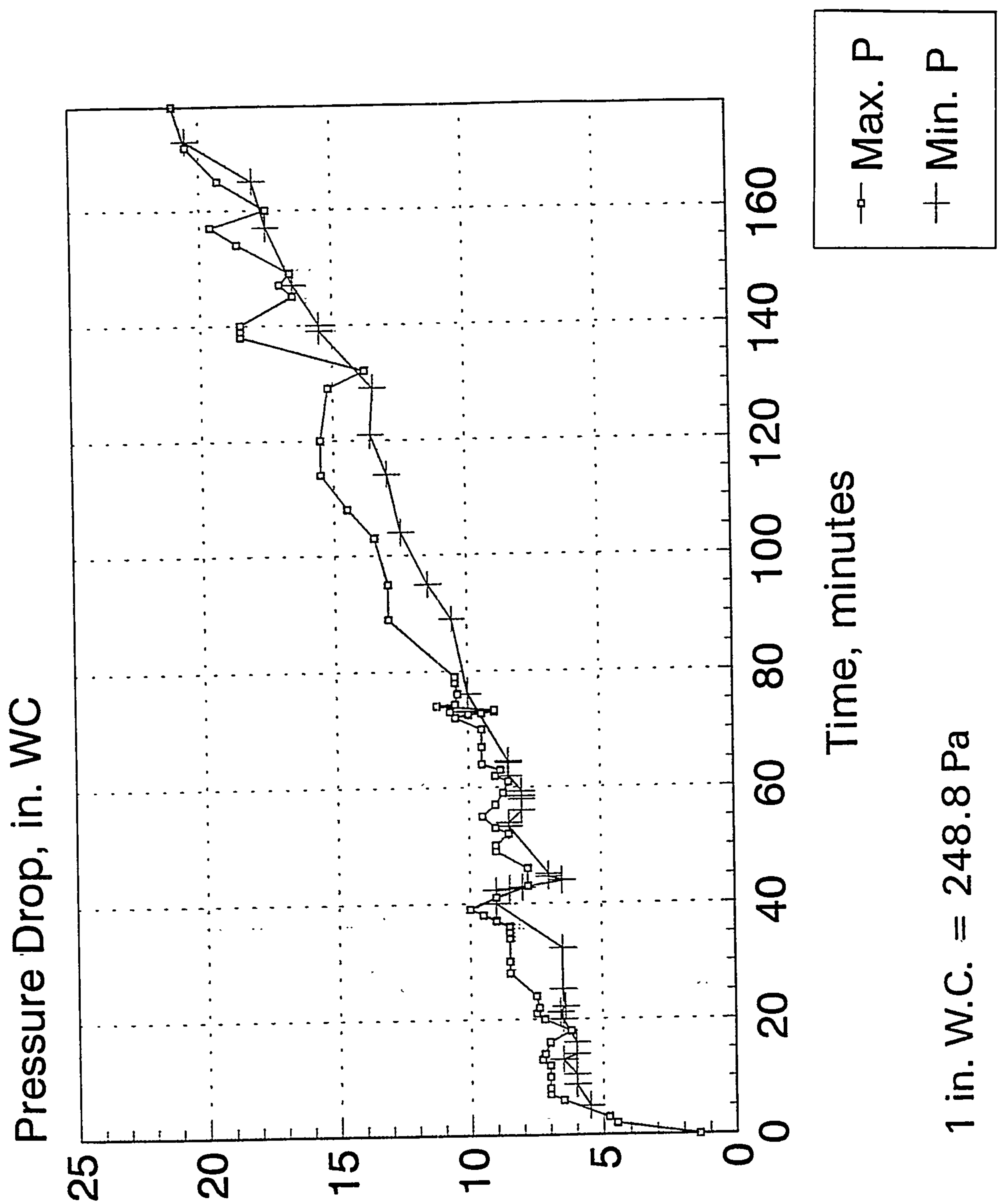

Figure 2. Baghouse Performance. Run 157--Switchgrass with Inconel filter.

down to change the coalescing filters, the transfer line between the vortex reactor and the char baghouse rapidly cools; the carrier gas must be turned on several minutes before the feed in order to preheat this transfer line; otherwise, the process stream could cool below the vapor dew point to create an aerosol that could sinter the char collected on the filter.

RUN 171 with flexible ceramic filters

This run used sugarcane bagasse from Louisiana for feed to produce a biocrude for the extraction of phenolics. The feeding rate was nominally 12 to 13 kg/h, with a nitrogen-carrier gas rate of 25 kg/h. The baghouse temperatures were measured to be 380 ± 10° C at the upper location, and 405° C to 430° C at the other two locations. As shown in Figure 3, we backflushed the bags on only four occasions during the first 98 minutes of operation. The first backflushing at 26 minutes involved all four bags and resulted in a pressure drop recovery from 3230 to 1245 Pa (13 to 5 in. W.C.). The second backflushing at 47 minutes involved only two bags to achieve a pressure drop recovery of from 3000 to 1680 Pa (12 to 6.75 in. W.C.). At 54 minutes, the system was temporarily shut down and all four of the bags were backflushed during this down time. After the system was restarted, the char was allowed to accumulate on the bags for 40 minutes before all four bags were backflushed to reduce the pressure drop from 4850 to 1370 Pa (19.5 to 5.5 in. W.C.).

This run demonstrated that we could allow a thick char cake to accumulate on the bags and still recover the same low pressure drop as that attained with more frequent backflushing. Longer periods between backflushing are recommended by the maker of the ceramic fabric filter for most effective filtration. The maker also recommended that some filter cake be left on the filter after backflushing, rather than trying to achieve the extremely low pressure drop of the initially clean filter; this was also demonstrated in this experiment.

DISCUSSION

Filter Media

To date, we have made three runs with the MEMTEC sintered Inconel filters and thirteen runs with the flexible, woven ceramic cloth filter bags made of Nextel. The rigid filters have been more difficult to backflush than the flexible bags, although good steady-state backflushing was achieved in Run 155. In the other two runs using the rigid filters, the pressure drop increased during the run. This pressure drop seemed to have increased in step-functions that tended to occur after the system had been shut down and restarted. This leads us to speculate that during the shut down process, the transfer line between the vortex reactor and the baghouse may have cooled. During restarting, the cooled transfer line may condense the vapor to form an aerosol that would have been collected on the filter cake. This collected aerosol would tend to sinter and plug the filter cake, making its removal difficult. It is important that the process vapors are not allowed even a momentary drop to below the temperature at which condensation begins. The flexible filter bag is able to expand and break the filter cake much better, so it appears to function better in this environment.

In discussions at NREL with 3-M Nextel representatives, they emphasized that the flexible-fabric bag will filter best with a thick filter cake on it (a high pressure drop). In at least two of the four runs made thus far with the Nextel bags, the measured pressure drop stayed very low during the run. This indicates that the filter cake was not accumulating on the flexible bag under certain operating conditions. It is speculated that momentary interruptions in the feeding or slugs of the feed dropping into the eductor jet may create pressure fluctuations of sufficient magnitude to cause the flexible bags

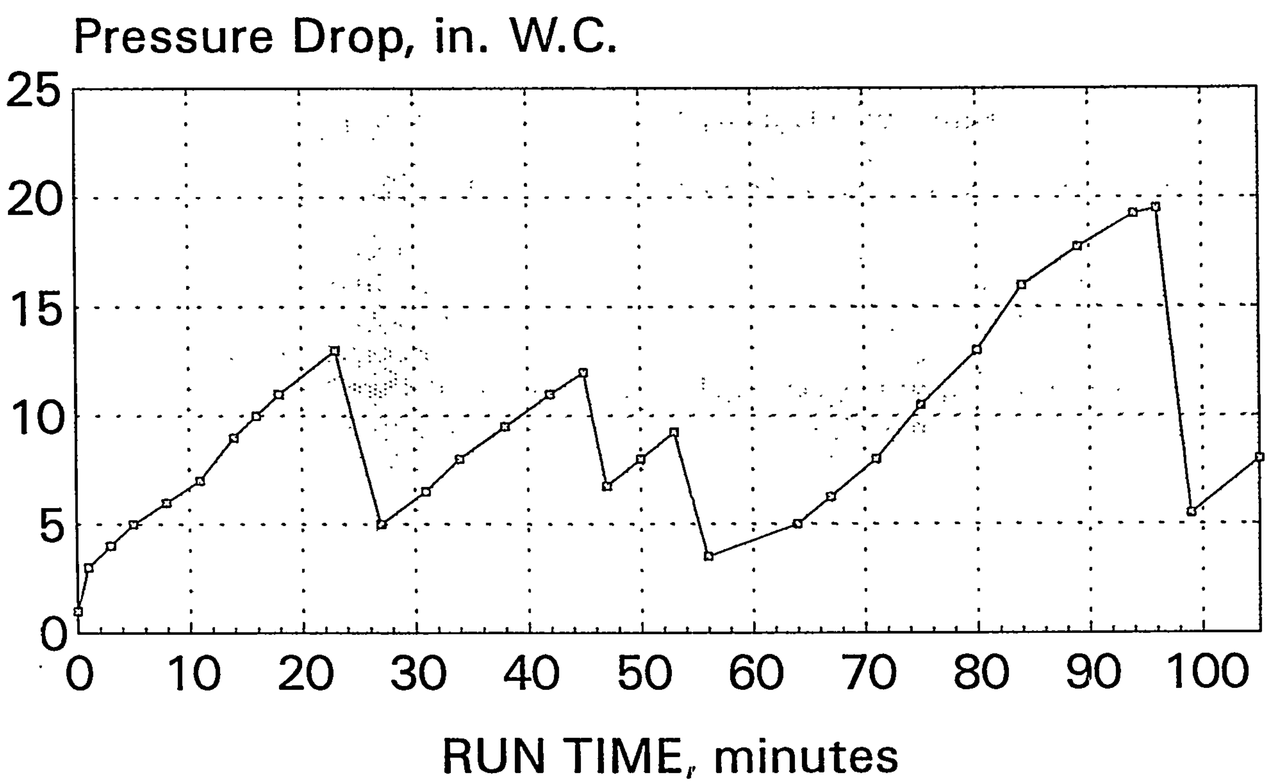

Figure 3. Baghouse Performance. Run 171--Bagasse with flexible ceramic filter.

to flutter. If the carrier gas is shut off, there could be a reversal of gas flow through the bag as the feed hopper is pressurized. If these events occur, the cake would be dislodged and would fall from the surface of the bag. Although this would keep the pressure drop conveniently low, the efficiency of the filtration would suffer if the filter cake did not accumulate. The 3-M representative suggested that we operate the Nextel filters with as high a pressure drop as we could allow, with backflushing only once an hour or so, if possible.

Removal of alkali contamination from oil

The reduction of alkali metals in biomass pyrolysis oils is one of the primary goals of our research in the Pyrolysis for Turbines task of the DOE Biomass Power Program. The current alkali limit for liquid turbine fuels is 1 ppm (wt) of alkali (ASTM D 2880). As shown in Table 1, the potassium, calcium, and sodium concentration in pyrolysis oils obtained from various feedstocks in the NREL vortex reactor with the use of cyclone separators greatly exceeded this level. Alkali concentrations were especially high in the oils obtained from switchgrass (740 ppm K, 490 ppm Ca, and 20 ppm Na).

In our current research, it has proven to be a difficult technical challenge to analyze the oils for alkali metal content. Previous attempts to analyze alkali content in biomass pyrolysis oils yielded inconsistent results. Analytical results from laboratories using the same measurement technique were different. Therefore, selection and development of a reliable method for determination of alkali metals content at the 1-ppm level was necessary to evaluate the pyrolysis oil quality and to develop techniques for hot-gas filtration.

To evaluate the analytical method quality and the reliability of a particular laboratory, we sent oil samples out to several laboratories: Huffman Labs, Hazen Research, Pacific Northwest Laboratory (PNL), Coors Analytical Laboratory, and the U.S. Geological Survey (USGS). The oils were also analyzed at NREL. Atomic Absorption spectroscopy (AA) was used by Huffman, Hazen, PNL, and NREL. Coors analyzed the oil by inductively coupled plasma emission spectroscopy (ICP). The USGS employed the method of neutron activation analysis.

Different methods were used to prepare samples for the AA analysis, based on the previous experience of the individual laboratories. Huffman prepared the samples by ashing, followed by dissolution in nitric acid. Hazen used direct digestion (dissolution in nitric acid and hydrogen peroxide), as recommended by the EPA for analyzing metals in water. PNL tested both ashing and digestion, while NREL analyzed the oil samples diluted in acetone. Each of these methods has certain drawbacks. Ashing can result in losses of the inorganic material because of its volatility or entrainment with combustion gases (smoke). Digestion requires larger amounts of acids (usually 50-100 times the amount of the sample) and this dilution can result in substantial error. Also, one cannot be certain that the whole sample was oxidized and dissolved. Possible heterogeneity, even in the presence of a good solvent like acetone, can also be a source of analytical error. In addition, contamination from dust in the laboratory could contribute to random errors. Most laboratories felt more confident working with samples that do not contain organics (which are said to interfere with the spectra). Round robin analyses of a biocrude oil made from oak with char removal by hot cyclonic separators resulted in 27-75 ppm K, 65-160 ppm Ca, and 2-100 ppm Na. Although the detection limits for K, Ca, and Na by AA are 0.1,.05, and 0.1 ppm, respectively, it appeared that the precision of the AA analysis was on the order of 10 ppm, which is not sufficient to develop the filtering techniques needed to meet the 1-ppm alkali requirement for the biocrude oil. Some of the problems with the reproducibility of the analyses are suspected to be due to heterogeneity of the oils themselves.

Coors Analytical Laboratory used ICP to determine the alkali content of the biocrude made from switchgrass in Run 157. Coors' technique involved digestion with nitric acid and hydrogen peroxide of six separate samples, which were then recombined before the final samples were taken for analysis. The analyses were done in triplicate and the resultant reproducibility was the best of the various laboratories. The Coors analyses also showed the lowest overall alkali content, as shown in Table 2.

The USGS in Golden, CO used a different analytical method for quantification of metals in the samples. With neutron activation analysis, samples and standards are irradiated in a reactor neutron flux and the induced radioactivity is measured using high-resolution gamma-ray spectrometry. A great advantage of this method is that it avoids the sample preparation step that probably contributes significantly to the error in AA analysis. The oil samples were irradiated for two minutes in a reactor having a neutron flux of 10^{12} neutrons/cm^2s, then analyzed (counting for 7 and for 30 minutes) using a germanium detector. Detection limits of this method are 1 ppm K, 2 ppm Ca, and 0.1 ppm Na.

The data presented in Table 2 illustrate the problem of reproducibility of alkali analyses with the biocrude oil made in Run 157, which used switchgrass as the feed and the sintered Inconel filters.

Inspection of the data shows that the indicated alkali contents varied by an order of magnitude, depending on the laboratory.

Table 1 compares the yields, ash content, and alkali content of the biocrude oils made from switchgrass and poplar. Table 1 also compares biocrude oils which had passed through two cyclone separators to oils made with the hot baghouse with either the rigid sintered filter or the flexible ceramic filter. Switchgrass is about five times higher in potassium and ash than is the poplar. The data in Table 1 show that passing the hot biocrude vapors through sintered Inconel filters produced an biocrude oil product with nearly two orders of magnitude less ash and alkali metals than when using the cyclone separators. The alkali content of the poplar-derived biocrude hot filtered through the flexible ceramic filters appears to be slightly higher, but within the same range as the switchgrass analyses. The alkali content of the hot-filtered biocrude oils appears to be higher than the goal of 1 ppm with either filter. However, based on the variability of the alkali analyses, it could be said that these hot-filtered oils are near or at the practical lower limit of detection with the existing state-of-the-art analytical techniques.

It is interesting to compare the values listed for the sum of the alkali metals for the hot filtered switchgrass biocrude, which in Table 2 ranged from 13 to 87 ppm alkali, to the total ash content of 100 ppm reported in Table 1. Because much of the ash in biomass consists of silica and since the alkalis would be present as compounds rather than in the elemental state, the reported values of alkali seem relatively high in comparison to the ash content. The analysis for alkali appears to need extensive additional development to provide reliable and reproducible results, if the fuel requirement of 1 ppm alkali is to be met with quality assurance results.

Cracking Severity--Temperature Effects

The biocrude oil produced in the initial operation of the baghouse seemed to be relatively low, even though we had operated our system at similar temperatures before. We had erroneously assumed that the rate of the cracking of the pyrolysis vapors to gases was relatively low at the conditions we were using in the baghouse. In Figure 4 is shown the effect of temperature for the existing baghouse with 91L (3.2 ft^3) of volume, for a baghouse with half that volume, and for the vortex reactor having a volume of 9.1L (0.32 ft^3). The volume of the transfer line between the vortex reactor and the baghouse was about the same as the vortex reactor. These curves are based on the extrapolation of the Arrhenius kinetic rates of the biocrude vapor cracking reaction (Diebold 1985). A gaseous flow rate of 0.27 gmol/s was assumed (31 ACFM at 752°F or 0.87 m^3/min at 400°C) for a gaseous residence time in the baghouse of 6 seconds. About 10% of the vapors are predicted to be converted to gases in the baghouse at 385°C and also in the vortex reactor at 510°C. Thus, for a system operating at these temperatures with an assumed initial yield of 69 wt% of primary vapors and 4 wt% prompt gases formed in the vortex reactor, 6.9 wt% would be converted to gas in the vortex reactor based on the vapors making one pass through the reactor. In the baghouse, of the remaining 61.1 wt% vapors, 6.1 wt% of them would also be converted to gases for a resultant oil vapor yield of 55 wt% and a gas yield of 17 wt%. Obviously lower temperatures and residence times would be advantageous for the preservation of the primary vapors.

The yields of pyrolysis oils (moisture-free basis) from Runs 155, 156, 157, and 160 were only in the range of 27-38 wt% of the feed. It is clear that the yields of oils theoretically and experimentally increase as the temperature of the baghouse is reduced. For example, dropping the baghouse temperature from 437°C-476°C in Run 155 to 386°C-405°C in Run 157 resulted in the dry-oil yield increasing from 27 to 38 wt% of the switchgrass feed. Some of this increase in yield may be attributed to a better mass closure, but the gas yields did drop with lower temperatures in the

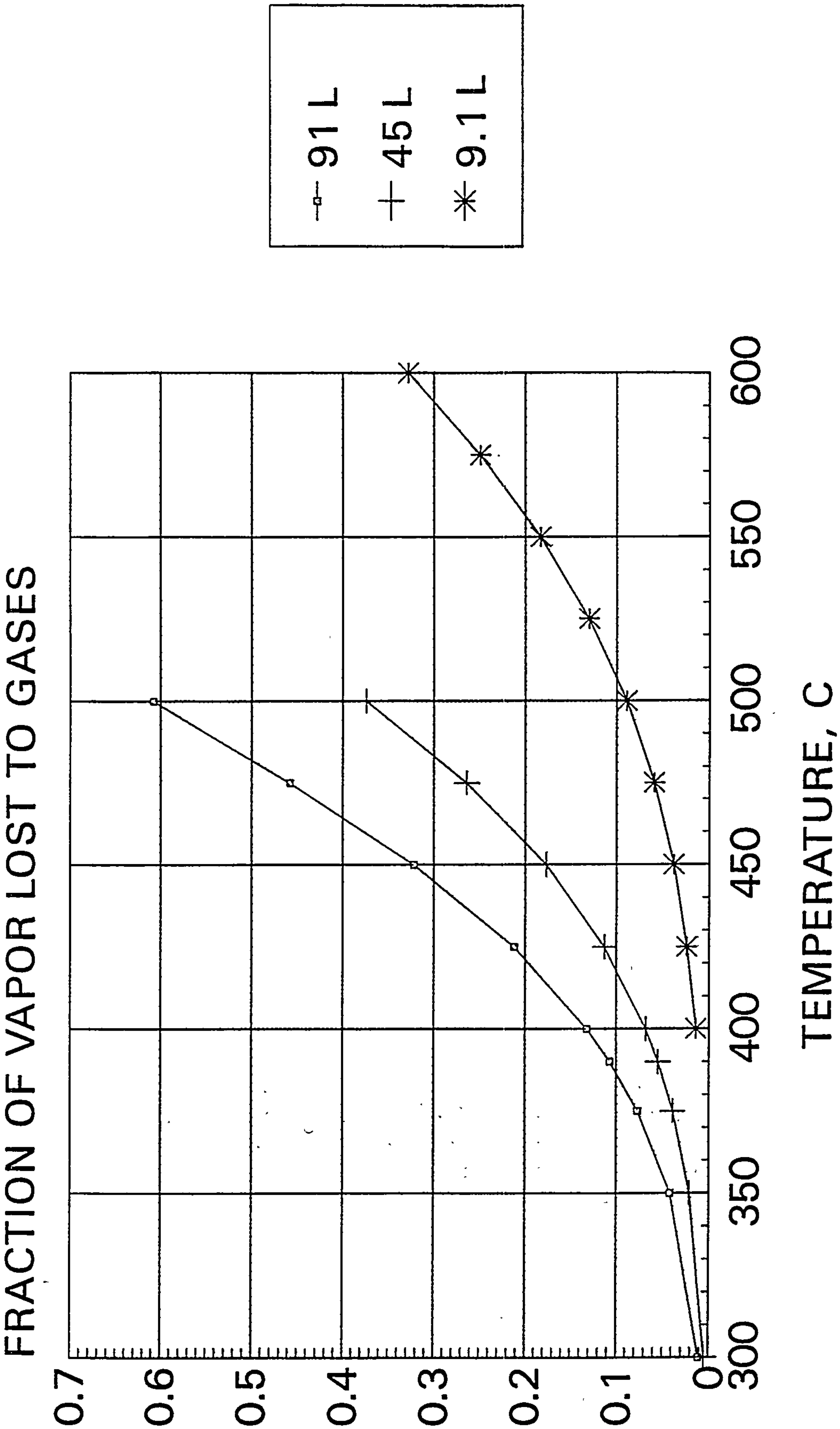

Figure 4. Biomass Vapor Loss. Based on kinetics from Diebold (1985).

baghouse. It is clear that the temperatures needs to be lowered further, but without condensing the vapors in the baghouse.

The thermocouple measuring the temperature of the baghouse is located near the top of the baghouse, touching the bag surface. This temperature is typically 40°C to 50°C lower than the temperature measured for the entering process-gas stream. The walls of the baghouse are independently heated by several heaters with their own thermocouples attached to the wall. It appears that the temperature history of the pyrolysis vapor, as it passes through the baghouse, is not adequately described by the single bag temperature. Ideally, the temperature of the process vapors would be isothermal and just above the dew point to avoid unnecessary vapor degradation. This implies that the temperature of the process stream entering the baghouse should be considerably lower than has been the case.

The vortex reactor has the potential of being a very low severity reactor, but it has not been pushed in this direction until very recently. The temperatures that we have been using for the vortex operation have evolved over the years to result in trouble-free operation. However, at the same time that we started the baghouse experiments, the system was significantly changed by the addition of more insulation, which has resulted in lower heat losses. In addition, the pyrolysis furnace was upgraded. As a result of these modifications, the vortex system seems to be running much hotter now than in the past with the same temperature set points. For example, whereas vortex reactor exit temperatures were around 500°C in the past, they were around 575°C during the first several experiments with the hot-gas filters. To reverse this trend, the temperature of the carrier gas has been gradually reduced in the last ten runs from 700°C to 450°C (made for the Biomass Adhesives Program and the Biofuels Program). The system appears to be operating well at these reduced temperatures and further reductions are planned in the future. As these temperatures are reduced, the amount of vapor cracking in the vortex reactor should be reduced and the vapor yields should increase significantly. We are planning a pyrolysis oil run in the near future to demonstrate the yields and the low alkali content with these new operating conditions.

In the vortex reactor, the heat for pyrolysis is supplied through the reactor wall directly to the biomass particle in sliding contact. The pyrolyzed biomass is thought to deposit as a liquid on the wall and then to undergo a combination of cracking and vaporization steps. The vapors immediately rise up off the wall to displace the lower-molecular-weight carrier gases. If enough solids are present on the wall to form a monolayer of particles, the pyrolyzing solids form a barrier to prevent further heat transfer to the vapors.

However, the high "g" field of the vortex reactor keeps the high-density vapors from freely mixing with the low density carrier gas stream. Some of the high- density vapors are thought to be recycled with the partially pyrolyzed solids through the tangential outlet and some are thought to escape from the vortex reactor directly through the axial outlet. The recycled vapors and solids are mixed vigorously in the eductor with the supersonic jet of the carrier-gas stream and are re-injected into the vortex reactor along with the new feed particles. The mixture of recycled vapors and carrier gas then leaves the vortex reactor through the axial exit after passing through the reactor. The relative amount of vapor recycled is not known, but an early experiment several years ago suggested that the minimum gas yield with no recycle was on the order of only 4 wt% of the feed that was pyrolyzed (Diebold, 1985). This visualization of the vortex reactor suggests that the carrier gas can act to quench the hot organic vapors to stop the rapid degradation reactions, or, conversely, to heat the vapors to accelerate the decomposition.

The temperature of the carrier gas undergoes a drastic reduction as it expands through the supersonic nozzle in the eductor. As the carrier gas is accelerated to supersonic speeds, part of the internal

energy of the gas is converted to kinetic energy. While the gases are at the very high velocities, part of their kinetic energy is transferred to the slower moving vapors and solid particles. As the gases slow due to internal friction, some of the remaining kinetic energy in the gases is recovered as thermal energy. This results in the fast moving, entrained gas, vapor, and solid stream having a lower temperature entering the reactor than if there had been no kinetic energy involved. The temperature of this entering stream must be merely high enough for the vapor/carrier gas mixture to be above the dew point of the vapors throughout the reactor.

This model implies that the temperature of the carrier gas can be further reduced to result in a pyrolysis stream exiting the vortex reactor around 400° C. The vortex reactor wall temperature will have to be adjusted so that the sliding, pyrolyzing particles on the reactor wall will form an effective heat-transfer barrier to the gas stream. This will require a very steady feeding rate so that the system will neither overheat the vapors nor plug the recycle loop with partially pyrolyzed particles. A process temperature above the minimum will need to be maintained for operability.
In the last several runs, we have been steadily lowering the temperature of our carrier gases to result in a lowering of the pyrolysis exit temperature and a subsequent lowering of the baghouse temperatures by about 5° C per run. We have added two additional thermocouples to measure temperatures within the baghouse and have observed 10°C to 40°C variations in the three temperatures measured; i.e., the baghouse interior is not isothermal (apparently due to heat losses). We have operated the baghouse successfully with local temperature excursions as low as 369° C (696° F) with relatively low ratios of carrier gases to feed without experiencing pyrolysis oil condensation or blinding of the flexible ceramic filters.

Cracking Severity--Residence Time Effects

Although an effort was made during the design phase to reduce the volume of the baghouse, there are some modifications that could be made to potentially achieve a significant reduction of the volume. Further analysis will suggest if these modifications are feasible.

The sum of these modifications would potentially result in a 50% reduction of the baghouse volume. However, the baghouse could become more difficult to backflush as the clearances between the filters and between the filters and the vessel walls are reduced. The reduction in volume translates directly to a reduction in the amount of vapor lost. To achieve a similar reduction in the vapor decomposed through a reduction in the reaction rate, the average temperature would have be lowered approximately 25° C. Consequently, we have been exploring lower-temperature operation as the key to reducing vapor cracking severity.

CONCLUSIONS AND RECOMMENDATIONS

The initial operation of the baghouse for the removal of char from the pyrolysis vapors has been very successful. The pressure drop through the filters has been relatively controllable with the use of periodic backflushing. Strategies for the backflushing are still under development and appear to be different for the two types of filters. Due to the very real possibility of vapor condensation on the filter and/or filter cake, operational procedures need to ensure that process upsets do not result in a momentary temperature drop of the process stream. This will be especially important as the operating temperature of the baghouse is progressively lowered to reduce the rate of decomposition of the organic vapors.

At this point, it is still unclear which filter media will prove to be the best. If the flexible filter bag is operated so that it has a sufficient permanent filter cake on it, the flexible bag has potential

advantages. Conversely, if we can learn how to avoid the step-change increases in the pressure drop seen with the rigid filters that are associated with momentary shut-downs, the rigid filter should filter the char out more completely. We have found that the flexible ceramic filters are much easier to backflush than the rigid filters and result in good pressure recoveries. In fact, very small pressure upsets tend to cause the filter cake to fall off the flexible ceramic filters.

Based on this work, it appears that all or nearly all of the alkali metal observed to be in the biocrude oil is present initially in the char fines carried over with the vapors. By removing these char fines, the alkali content of the oil is drastically reduced to such a low level that analytical techniques need to be improved to adequately quantify it. However, the variability of the alkali analyses has been blamed on possible heterogeneity of the samples. With future decreases in operating temperatures (and consequently the cracking severity in the vortex reactor and the baghouse), the oils should become more homogeneous and also present in higher yields.

The pyrolysis system needs to be operated closer to the minimum temperatures possible to maximize the survival of the pyrolysis oil vapors. This would ideally have the pyrolysis stream exiting the vortex reactor at about 400° C. Operation at progressively lower temperatures will entail some risk of plugging the recycle loop with the resultant flow of partially pyrolyzed biomass to the baghouse, as well as partial pluggage of the filter media. However, the current low yield of organic condensates with the baghouse suggests that this experimentation is very necessary. We have continued to lower the operating temperatures in small incremental changes to avoid compromising other experimental goals. This work is still in progress, but we hope to learn the lower temperature limit of operation with a smaller pyrolysis experiment now coming on line.

The volume of the baghouse could be reduced with additional design effort, further reducing the loss of vapors. However, as shown in Figure 4, if the average temperature in the baghouse can be reduced to 400° C or lower, the effect of the proposed reduction in volume would be only about 5% more organic condensates (compared to 14% more at 450° C). Realistically however, the ratio of relative volume to the filter area of the current baghouse is similar to what would be scaled up using current baghouse technology.

SUMMARY

It is clear that the separation of char from pyrolysis vapors is of utmost importance in producing a premium-quality pyrolysis oil product. Experience has shown that cyclonic separators are marginal for this purpose and do not scale up well. Filtering of the acidic oil to remove particulates does not appear promising to remove the acid-soluble alkali contaminants. Ongoing development at NREL is showing the promise of hot-gas filtering for this purpose, but is also pointing to pitfalls to be avoided. In particular, the alkali analyses are very difficult to achieve accurately at the low alkali levels of interest. It is the intent of this effort at NREL to continue to explore the variables that affect the efficient operation of a baghouse to remove particulates from this chemically reactive pyrolysis vapor stream.

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Table 1. Performance of Cyclone Separators and Baghouse Filter Media

------------ Switchgrass ------------------ ------ Poplar ----

	Run 146B Switch-grass Feed	Run 146B Two cyclones in series* Biocrude Oil	Run 157 Switch-grass Feed	Run 157 Baghouse w/ Inconel Filters Biocrude Oil	Run 160 Poplar Feed	Run 160 Baghouse w/ Flexible ceramic filter Biocrude Oil
wt% Yields						
Dry Oil	NA	37.0	NA	37.6	NA	35.8
Char	NA	19.9	NA	21.8	NA	11.7
Gas	NA	24.6	NA	19.5	NA	23.6
Water	NA	14.2	NA	16.1	NA	16.1
Total	NA	95.7	NA	95.0	NA	87.4
Ash, wt%	6.0	0.95	5.66	0.01	1.00	0.005
, ppm	60000	9500	56600	100	10000	50
K,ppm	5000	1380	8250	1-15	1650	7-30
Ca	3300	660	2860	3-47	2500	20-50
Na	34	40	70	5-30	50	2-30

*medium cracking severity conditions in the vapor cracker

Table 2. Alkali concentration in Switchgrass Biocrude Oil (Run 157)

Laboratory	Potassium, ppm	Calcium, ppm	Sodium, ppm
Hazen	15	42	30
Huffman	<10	<5	<5
NREL	0	3	12
Coors	1	6	6
U.S. G.S.	14	6	2

ENGINEERING DEVELOPMENTS IN FAST PYROLYSIS FOR BIO-OILS

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ABSTRACT

Biomass pyrolysis is of rapidly growing interest in Europe while in North America, interest seems to have peaked a few years ago. This paper has three objectives:

1. To review the R,D&D in biomass fast pyrolysis in Europe supported by the European Commission.
2. To review the problems faced by the developers of fast pyrolysis, upgrading and utilisation processes which require resolution if the technologies are to be implemented.
3. To summarise the current status of fast pyrolysis activities.

Approximately US$ 5 million per year are being spent by the European Commission (EC) on R&D in thermal biomass conversion of which pyrolysis receives the lions share. Funding comes from a variety of EC R&D programmes (AIR, JOULE and APAS). The demonstration programmes (THERMIE and ALTENER) have yet to support any pyrolysis projects. A new 5 year Framework Programme started in January 1994 valued at US$ 15 billion in which bioenergy may receive over 150 US$million In addition most countries in the EC have their own bio-energy R&D programmes which are usually complementary to the EC programmes. Aspects of design of a fast pyrolysis system include feed drying; particle size; pretreatment; reactor configuration; heat supply; heat transfer; heating rates; reaction temperature; vapour residence time; secondary cracking; char separation; ash separation; liquids collection. Each of these aspects is reviewed and discussed. Finally the current status of the main fast pyrolysis activities around the world is summarised.

INTRODUCTION

Biomass fast pyrolysis is of rapidly growing interest in Europe. Approximately US$ 5 million per year are being spent by the European Commission (EC) on research and development in the area of thermal conversion, of which pyrolysis receives the largest proportion. Funding comes from the EC R&D programmes in the form of AIR (Agro-Industrial Research) programmes, the JOULE (Joint Opportunities for Unconventional and Long term Energy in Europe) programmes and the recent APAS programme. There are also EC Demonstration activities in the form of the THERMIE and ALTENER programmes which have not yet supported any fast pyrolysis projects but which would be expected to provide demonstration of successful projects from the above R&D programmes. A new 5 year Framework Programme started in January 1994 with a total R&D budget of around US$ 15 billion of which around US$ 2-2.5 billion is notionally allocated to renewable energies and agro-industrial research. The bioenergy sector may receive around US$ 150 million. In addition most countries in the EC have their own bio-energy R&D programmes which are usually complementary to the EC programmes.

PYROLYSIS CONCEPTS

Principles

Biomass is a mixture of hemicellulose, cellulose, lignin and minor amounts of other organics which each pyrolyse or degrade at different rates and by different mechanisms and pathways. Lignin decomposes over a wider temperature range compared to cellulose and hemicellulose which rapidly degrade over narrower temperature ranges, hence the apparent thermal stability of lignin during pyrolysis. The rate and extent of decomposition of each of these components depends on the process parameters of reactor (pyrolysis) temperature, biomass heating rate and pressure. The degree of secondary reaction (and hence the product yields) of the gas/vapour products depends on the time-temperature history to which they are subjected to before collection which includes the influence of the reactor configuration. Although some research has been carried out on the individual components of biomass, most applied and larger scale work has focused on whole biomass as the cost of pre-separation is considered too high. In addition, the separation and recovery of pure forms of lignin and hemicellulose are difficult due to structural changes in their processing, although pure cellulose is relatively easy to produce.

Research has shown that maximum liquid yields are obtained with high heating rates, at reaction temperatures around 500°C and with short vapour residence times to minimise secondary reactions. Fast pyrolysis processes have been developed for production of food flavours (to replace traditional slow pyrolysis processes which had much lower yields) and speciality chemicals which utilise very short vapour residence times of typically 100-300 ms and reactor temperatures around 500°C. Both residence time and temperature control is important to "freeze" the intermediates of most chemical interest in conjunction with moderate gas/vapour phase temperatures of 400-500°C before recovery of the product to maximise organic liquid yields.

Liquids for use as fuels can be produced with longer vapour residence times [up to ~6 s] and over a wider temperature range although yields might be affected in two ways: secondary gas decomposition at temperatures above 500°C and condensation reactions at gas/vapour product temperatures below 400°C. Most woods give maximum liquid yields of up to 80% wt% dry feed basis [64 wt% organics and 16 wt% water] at 500-520°C with vapour residence times not more than 1 second. Very short residence times result in incomplete depolymerisation of the lignin due to random bond cleavage and inter-reaction of the lignin macromolecule resulting in a less homogenous liquid product, while longer residence times can cause secondary cracking of the primary products, reducing yield and adversely affecting bio-oil properties. Evidence from SEC analysis of the liquids would suggest that the reactor configuration and the dominant mode of heat transfer strongly influences the average molecular weight of the products (1). This is discussed further below.

PROCESS CHARACTERISTICS AND TECHNOLOGY REQUIREMENTS

Although fast pyrolysis of biomass has achieved commercial status, there are still many aspects of the process which are largely empirical and require further study to improve reliability, performance, product consistency, product characteristics and scale-up. This section summarises these topics.

Reactor configuration

A variety of reactor configurations have been investigated as listed in Table 1. Pyrolysis, perhaps more than any other conversion technology, has received considerable creativity

and innovation in devising reactor systems that provide the essential ingredients of high heating rates, moderate temperatures and short vapour product residence times for liquids.

Heat transfer

There are two important requirements for heat transfer in a pyrolysis reactor:
1 to the reactor heat transfer medium (solid in ablative reactor, gas and solid in fluid and transport bed reactors, gas in entrained flow reactors),
2 to the pyrolysing biomass.

Two main ways of heating biomass particles in a fast pyrolysis system can be considered: gas-solid heat transfer as in an entrained flow reactor where heat is transferred from the hot gas to the pyrolysing biomass particle by primarily convection (for example the Egemin process), and solid-solid heat transfer with mostly conductive heat transfer. Fluid bed pyrolysis utilises the inherently good solids mixing to transfer approximately 90% of the heat to the biomass by solid-solid heat transfer with a probable small contribution from gas-solid convective heat transfer of up to 10%. Circulating fluid bed and transport reactors also rely on both gas-solid convective heat transfer from the fluidising gas and solid-solid heat transfer from the hot fluidising solid although the latter may be less significant than fluid beds due to the lower solids bulk density. Some radiation effects occur in all reactors.

Table 1 Pyrolysis Reactors, Heating Methods and Heating Rates

Reactor type	Method of Heating	Organisation
Ablative cone	Wall and sand heating	U.Twente
Ablative mill	Wall (disc) heating	CSM
Ablative plate	Wall heating	U.Aston, U.Nancy
Ablative vortex	Wall heating	NREL, Interchem
Auger kiln	Wall heating	U.Tubingen, WTC
Circulating fluid bed	In-bed gasification of char to heat sand	CRES
Cyclone or vortex	Wall heating	See *Ablative vortex*
Entrained flow	Combustion products	Egemin, GTRI
	Hot sand	U.Western Ontario ¶
Fixed bed	Combustion products	Bio-Alternative
	Partial gasification	Alten §
Fluid bed	Heated recycle gas	INETI, Union Fenosa, U.Waterloo, Worthing
	Hot inert gas	CPERI, NREL, U.Aston, U.Leeds, U.Sassari,
	Partial gasification	Alten §
	Fire tubes	MTCI ¶
Horizontal bed	Fire tubes	Pyrosol*
Multiple hearth	Hearth heating	U.Laval
Rotary kiln	Wall heating	Deutsche Babcock*, KWU*, PKA*, Stenau*
Stirred bed	Partial gasification	Alten §
Transported bed with solids recirculation	Hot sand and gas	Ensyn

NOTES
* Used for solid waste processing, not liquids production
¶ Used for gas production
§ Operational mode unclear

The important feature of ablative heat transfer is that the contact of the biomass and the hot solid abrades the product char off the particle exposing fresh biomass for reaction. This removes particle size limitations in certain ablative reactors (e.g. the NREL vortex reactor). Attrition of the char from the pyrolysing particle can also occur in both fluid and circulating fluid beds, due to contact of the biomass with in-bed solids where solids mixing occurs. In fluid bed reactors however, attrition of the product char is relatively low and it has been observed that the char particles have the original particle shape, but are slightly reduced in size by char layer shrinkage and attrition.

Char removal is an essential requirement for large particles (> 2 mm) to avoid slow pyrolysis reactions from the low thermal conductivity of biomass giving low heating rates through larger particles which leads to increased char formation. Hot char is known to be catalytically active. It cracks organic vapours to secondary char, water and gas both during primary vapour formation and in the reactor gas environment, therefore it's rapid removal from the hot reactor environment and minimal contact with the pyrolysis vapour products is essential.

Since the thermal conductivity of biomass is very poor (0.1 W/mK along the grain, ca 0.05 W/mK cross grain), reliance on gas-solid heat transfer means that biomass particles have to be very small to fulfil the requirements of rapid heating to achieve high liquid yields. Claimed temperature increases of 10,000°C/s may be achieved at the thin reaction layer but the low thermal conductivity of wood will prevent such temperature gradients throughout the whole particle. As particle size increases, liquid yields reduce as secondary reactions within the particle become increasingly significant (2). Union Fenosa are using particle sizes of smallest dimension 2 mm in their 200 kg/h fluid bed to achieve total liquid yields of around 55% wt. on dry feed with a 15% water content (3). Ensyn claim that particle sizes of up to 5-6 mm in their reactor will still give total liquid yields of up to 75% wt. on feed with 10% moisture which is equivalent to 83% wt. on dry feed basis. Based on the original vortactor work at the University of Western Ontario, it seems likely that attrition of particles at the base of the Ensyn RTP reactor would be a feature of their system to remove char from the particle surface with some degree of solid-solid heat transfer. Egemin found with their entrained reactor that particle sizes of 6 mm caused a large proportion to be expelled from the reactor substantially unreacted due to poor heat transfer and no char removal from ablation. This resulted in total liquids yields of less than 40% wt on dry feed (4), while GTRI claimed yields of over 60% total liquids with an up flowing entrained flow reactor using feed sizes up to 6 mm (5).

A consistent method of expressing product yields is required to remove ambiguities in the comparison of product yields. It is recommended that the water in the feed should be discounted in the final pyrolysis products with only the water of pyrolysis being quoted and the product yields expressed on a dry feed basis. As a rule of thumb, the water of pyrolysis is typically 11 wt% of dry feed.

Heat supply

The high heat transfer rate that is necessary to heat the particles sufficiently quickly imposes a major design requirement on achieving the high heat fluxes required to match the high heating rates and endothermic pyrolysis reactions. Reed et al. originally suggested that to achieve true fast pyrolysis conditions, heat fluxes of 50 W/cm^2 would be required but to achieve this in a commercial process is not practicable or necessary (6).

Each mode of heat transfer imposes certain limitations on the reactor operation and may increase its complexity. The two dominant modes of heat transfer in fast pyrolysis

technologies are conductive and convective. Each one can be maximised or a contribution can be made from both depending on the reactor configuration. The penalties and interactions are summarised in Table 2 below with some speculations on heat transfer modes.

For ablative pyrolysis in a vortex reactor, a furnace arrangement equivalent to an ethylene cracking furnace has been proposed by the IEA Bioenergy Agreement pyrolysis and liquefaction group (7, 8). Other possibilities to achieve the pyrolysis temperatures and heat transfer rates necessary have included vapour condensation such as sodium, induction heating of the reactor wall and the use of contact electrical heaters. In a circulating fluid bed, the majority of the heat transfer will be from the hot circulating sand which therefore requires an efficient sand re-heating system. In a conventional fluid bed the sand requires an external heat source.

A commercial system would be expected to utilise the by-product char and gas for the process heat requirements as an integrated system as proposed for the NREL wood to gasoline process evaluated by the IEA (7, 8).

Table 2 Reactor Types and Heat Transfer

Reactor type	Suggested mode of heat transfer	Advantages/disadvantages/features
Ablative	95% Conduction 4% Convection 1% Radiation	Accepts large feedstocks; Good mechanical char abrasion; Solids decoupled from gas products; Compact design; Heat supply problematical; Heat transfer gas not required; Particulate transport gas not always required.
Circulating fluid bed	80% Conduction 19% Convection 1% Radiation	Limited char abrasion; High heat transfer rates; Char/solid heat carrier separation required; Simultaneous char combustion to heat solids; Solids recycle required; Increased complexity of system; Maximum particle sizes up to 6 mm; Possible liquids cracking by hot solids; Possible catalytic activity from hot char; Reactor wear can occur.
Fluid bed	90% Conduction 9% Convection 1% Radiation	High heat transfer rates; Very good solids mixing; Particle size limit <2 mm in smallest dimension; Simple reactor configuration.
Entrained flow	4% Conduction 95% Convection 1% Radiation	Low heat transfer rates; Particle size limit <2 mm; Limited gas/solid mixing.

Feed preparation

The heat transfer rate requirements described above impose particle size limitations on the feed for some reactors. The cost of size reduction in financial and energy terms is clear qualitatively but data is not available to define such a penalty associated with the small particle sizes demanded of fluid bed and circulating fluid bed systems. Reactor performance as for example liquid yields is, therefore, not an adequate criterion by itself.

Drying is usually required to less than 10% wt water unless a naturally dry material such as straw is available. As moisture is generated in flash pyrolysis, bio-oil always contains at least about 15% water at an assumed product yield of around 60 wt% organics and 11 wt% reaction water. This water cannot be removed by conventional methods such as distillation. The effect of water is complex in that it affects stability, viscosity, pH, corrosiveness, and other liquid properties. Selective condensation may reduce the water content of one or more fractions but at the expense of operating problems and a possible loss of low molecular weight volatile components.

Temperature of reaction

It is necessary to distinguish between temperature of reaction and reactor temperature. The latter is much higher due to the need for a temperature gradient to effect heat transfer. For fast pyrolysis the lower limit on wood decomposition is approximately 435°C for obtaining acceptable liquid yields of at least 50% with low reaction times.

The effect of temperature is well understood in terms of total product yield with a maximum at typically 500-520°C for most forms of woody biomass. Other crops may have maxima at different temperatures. The effect of temperature is less well understood in terms of product fuel quality. Work by the University of Waterloo has demonstrated the effects of ash, DP, heating rate and reactor temperature on chemical yields (9). As progress is made in defining bio-oil quality better in fuel terms, the secondary gas/vapour phase history may be more important. At prolonged residence times (> 1 s), the lignin derived fraction may be further depolymerised to produce a more homogeneous liquids. This is also influenced by the reactor configuration. Work done by McKinley (1) has demonstrated that liquid produced in an ablative pyrolysis reactor has a much lower molecular weight average due to depolymerisation and cracking of the liquids on the metal surface prior to vaporisation.

Vapour residence time

The effect of vapour residence time on organic liquid yield is relatively well understood although the interaction of temperature and residence time is less understood. Studies by Diebold et al., Liden et al and Knight et al. have attempted to interlink both primary liquids formation and secondary cracking, but one essential component which is neglected is the variation of water yield with temperature and residence time. It is believed that at temperatures below 400°C, secondary condensation reactions occur and the average molecular weight of the liquid product decreases. Boroson et al. have demonstrated that the average molecular weight decreases with the degree of secondary reaction, i.e. increasing residence time and temperature (10).

For chemicals, it is considered necessary to "freeze" the process at the appropriate time-temperature point in the envelope to maximise yield. In one case this has led to a commercial reactor design where vapour residence times down to 90 ms are claimed.

Fuels have less specific process requirements and most work has focused on maximising liquid yield rather than product quality.. The window for fuel production requires more

R&D to better understand the processes and match the product quality requirement to process parameters. There is no definition of product quality in terms of physical or chemical properties or composition, and this area will need to be addressed as more applications are tested and alternative supplies of bio-fuel-oil become available.

Secondary vapour cracking

Long vapour residence times and high temperatures (> 500°C) cause secondary cracking of primary products reducing yields of specific products and organic liquids. Lower temperatures (< 400°C) lead to condensation reactions and the subsequent formation of lower molecular weight liquids which can also react.

Liquids collection

This has long been a major difficulty for researchers. The pyrolysis vapours have similar properties to cigarette smoke and capture by almost all collection devices is very inefficient. The product vapours are not true vapours but rather a mist or fume and are typically present in an inert gas at relatively low concentrations which increases cooling and condensation problems. They can be characterised as a combination of true vapours, micron sized droplets and polar molecules bonded with water vapour molecules. This contributes to the collection problem as the aerosols need to be impinged onto a surface to permit collection, even after cooling to below the dew point temperature.

Electrostatic precipitators are effective but can create problems from the polar nature of the product and arcing of the liquids as they flow, causing the electrostatic precipitator to short out. Larger scale processing usually employs some type of quenching or contact with cooled liquid product which is effective. Careful design is needed to avoid blockage from differential condensation of heavy ends. The rate of cooling appears to be important. Slow cooling leads to preferential collection of the lignin derived components which is a viscous liquid which can lead to blockage of heat exchange equipment and liquid fractionation. Very rapid cooling of the product has been suggested to be effective as occurs typically in a direct contact quench. Transfer lines from the reactor through the cyclone(s) to the liquid collection system should be maintained at > 400°C to minimise liquid deposition and collection.

At present, there are no recognised design methods and most work has been empirical and specific to the characteristics of the feedstock being processed. Commercial liquids recovery processes are usually proprietary and may be specific to individual feedstocks and reactor configurations/.

Char separation

Some char is inevitably carried over from cyclones and collects in the liquid. Subsequent separation has proved difficult. Some success has been achieved with hot gas filtration in a ceramic cloth bag house filter (11) and also candle filters for short run durations. Liquid filtration has also proved difficult as the liquid can have a gel-like consistency, apparently due to some interaction of the lignin-derived fraction with the char.

This aspect of char reduction and/or removal will be increasingly important as more demanding applications are introduced which require lower char tolerances in terms of particle size and total quantity. Possible solutions include changing process conditions to reduce the nature of the pyrolytic lignin, increasing the degree of depolymerisation of the lignin-derived fraction of the liquid, changing the feedstock to one with a lower lignin

content, or adding chemicals to the liquid for example to improve handling properties or reduce char-lignin interactions.

It must not be forgotten that an alternative solution is to modify the application to accept a high char content bio-fuel-oil.

Ash separation

The alkali metals from biomass ash are present in the char in relatively high concentrations and cannot be readily separated except by hot gas filtration which is undergoing development as reported variously in these proceedings.

PRODUCT CHARACTERISTICS

Product quality

The complex interaction of time and temperature on liquid product quality has not been explored, at least partly because the characteristics of pyrolysis oil for different applications has not been defined and there is no "standard" pyrolysis liquid. It is this definition of oil quality that is a major uncertainty and requires to be defined by potential users and may differ by application. While there are set standards and methods of measurement for conventional fuels, analogous standards and methods have not yet been defined for biomass pyrolysis liquids. Density, viscosity, surface tension and heating value are known to be typical key properties for combustion applications in boilers, furnaces and engines; but other characteristics such as char level and particle size and ash content may have a major effect.

Unusual characteristics

Bio-fuel-oil has a number of special features and characteristics which require consideration in any application including production, storage, transport, upgrading and utilisation. These are summarised in Table 3 below. The conclusion is that some problems are soluble and some are more intractable but none are insoluble. Recognition of problems and awareness of potential difficulties is a major contribution to dealing with any of the above difficulties.

PYROLYSIS PROCESSES

A brief overview of the current position on fast pyrolysis processes for liquids is given below. A recent review of processes that are advanced technically and/or commercially available has been published (12).

North America

Fast pyrolysis of biomass for liquids began in North America around 1980 and has seen significant RD&D effort since then with one successful commercial organisation offering plants with a performance guarantee and several demonstration and pilot scale processes.

<u>Ensyn</u>

Ensyn's RTP technology evolved from the research on fast pyrolysis carried out at the University of Western Ontario. They are still the only commercial organisation selling fast pyrolysis plants with a performance guarantee. There are three operational plants: a 25 dry te/d unit at Red Arrow in Wisconsin and an 80 kg/h unit and 10 kg/h R&D unit in Ottawa.

Six plants are currently at a design or construction stage: 60, 25, 25, 15, 7.2 and 1 dry te/d which includes the 15 t/d unit for ENEL in Italy for delivery in 1995. Further plants for fuel production are in advanced negotiation in the USA. Ongoing development work includes hot vapour filtration to reduce ash and char, liquid filtration to reduce char, supply of oil for engine and turbine testing in Canada and Europe, combustion testing, upgrading and product characterisation.

Table 3 Characteristics of Bio-oil and Methods for Modification

Characteristic	Effect	Solution
Suspended char	Erosion, Equipment blockage, Combustion problems from slower rates of combustion. "Sparklers" can occur in combustion leading to potential deposits and high CO emissions.	Hot vapour filtration; Liquid filtration; Modification of the char for example by size reduction so that its effect is reduced; Modification of the application.
Alkali metals	Deposition of solids in combustion applications including boilers, engines and turbines. In turbines the damage potential is considerable particularly in high performance machines with, for example, coated blades.	Hot vapour filtration; Processing or upgrading of oil; Modification of application; Pretreat feedstock to remove ash
Low pH	Corrosion of vessels and pipework.	Careful materials selection; Stainless steel and some olefin polymers are acceptable
Incompatibility with polymers	Swelling or destruction of sealing rings and gaskets.	Careful materials selection.
Temperature sensitivity	Liquid decomposition on hot surfaces leading to decomposition and blockage; Adhesion of droplets on surfaces below 400°C.	Recognition of problem and appropriate cooling facilities; Avoidance of contact with hot surfaces > 500°C.
High viscosity	High pressure drops in pipelines leading to higher cost equipment and/or possibilities of leakage or even pipe rupture.	Careful low temperature heating, and/or addition of water, and/or addition of co-solvents such as methanol or ethanol.
Water content	Complex effect on viscosity, heating value, density, stability, pH, homogeneity etc.	Recognition of problem; Optimisation with respect to application.
In-homogeneity	Layering or partial separation of phases; Filtration problems.	Modify or change process; Modify pyrolysis parameters; Change feedstock to low lignin; Additives; Control water content.

NREL

NREL have been developing their 36 kg/h vortex ablative pyrolyser since 1980. Designs for scale up have been produced and support has been provided to Interchem for the reactor in their 31 te/d demonstration plant (see below). A second R&D unit has now been constructed and a small fluid bed fast pyrolysis unit has also been commissioned. . Zeolite upgrading of the pyrolysis vapours to aromatics has been accomplished at the fundamental level on the MBMS system, on a slip-stream of the vortex reactor and on the full reactor output. Novel multi-functional zeolite catalysts have been produced and tested. A circulating fluid bed zeolite cracker with regenerator is under construction. Only limited results have been published on any of this work including recent work by Czernik et al. (13) on vapour phase thermal treatment to lower the oxygen content of the liquid.

Interchem

The 31 te/d demonstration plant was moved from Mountain View Missouri to Kansas City and the reaction system completely redesigned with the support and assistance of NREL (14). The construction of the new reactor was completed in late summer 1993 and work has now stopped on the project. Future plans are unclear.

BBC

A 10-25 kg/h unit was constructed to investigate the reactor parameters of surface temperature and gas/vapour product residence time and particle size. Although the unit was built to pyrolyse tyres, it is capable of using wood, MSW and other similar materials as a feedstock. Limited details of the continuous ablation reactor are available (15). Particles up to 6 mm have been used with liquid recovery in a two stage direct liquid quench of the product vapours with recycled liquids after char removal in a high temperature cyclone. Liquids are collected in a sump tank and are returned to quench the hot vapours via a water cooled heat exchanger. Liquid yields of 54% have been obtained from tyres at 470-540°C at 0.88 s residence time and 1.3 mm size particles (16). A 35-50 t/d plant has been built in Nova Scotia where it is operating successfully with combustion of the raw product gas and no liquids collection.

University of Waterloo

This program was initiated in 1979 with the main objective of establishing conditions for maximising liquid yields from biomass, particularly from forest materials. The University of Waterloo can be credited with the foundation of modern fast pyrolysis and their research is probably the most extensively published and publicised in this area. Two fluid bed reactors are used of 100 g/h and 3 kg/h. The results from these units were used to design a 200 kg/h unit for Union Electrica Fenosa in Spain as described below. Temperatures of 400-700°C have been examined with a wide range of feedstocks, pretreatment methods, various inert and reactive gases and some work on in-bed catalysts. The fluid beds were designed in a blow-through mode to entrain the char from the bed while retaining the sand hence there is no need for sand circulation or replacement. The highest yields of total liquid product are around 70 wt% on dry feed and are typically obtained at temperatures around 500°C.

Worthing Industries

A 200 kg/h fluid bed reactor derived from the University of Waterloo work was originally constructed in 1986 by Encon for wood and peat pyrolysis. The unit was constructed on the back of a trailer for transportation to test sites for demonstration. This is now used for

processing old telegraph poles . These have their outer skin of treated wood removed and which is then pyrolysed in a 50 kg/h fluid bed pyrolyser for recovery of chemicals including creosote and PCP as well as bio-oil. Up to 30,000 poles per year are processed. The skimmed poles are re-treated and recycled (17).

Other activities

More fundamental studies are being carried out in several laboratories including the University of Hawaii (18) and the University of Montana (19).

Europe

In Europe the situation is more varied but less developed with only one substantial pilot plant. Most interest has been stimulated by the EC JOULE and AIR programmes over the last 8 years.

CPERI (Greece)

A small fluid bed reactor has been operating for several years to provide pyrolysis liquids (20) from which phenols and related chemicals are recovered for production of oxygenates such as methyl aryl ethers for use as gasoline additives (21).

The Centre for Renewable Energy Sources (CRES) and the Agricultural University of Athens (Greece)

A circulating fluid bed fast pyrolysis system has been designed, built and commissioned. Fast pyrolysis is carried out in the riser of a CFB using reheated sand and hot combustion products from burning char in a bubbling fluid bed at the base of the riser (22). Although the reactor system works well, liquid product collection is problems are still being resolved. The process is described in these proceedings.

Egemin (Belgium)

This 200 kg/h capacity entrained downflow system was commissioned in 1991 and operated at up to around 50 kg/h giving liquid yields around 45% wt. (4). It was closed down permanently in 1992 due to unpromising results from the unit and lack of further support from the EC. It is unlikely to be restarted.

ENEL (Italy)

A contract has been signed to purchase a 650 kg/h Ensyn RTP-III plant (transported bed reactor) employing recycle gas (23). This will be commissioned around September 1995. The bio-oil product will be tested in a variety of applications including firing in a power station boiler, upgrading by hydrotreating and firing both an engine and turbine.

INETI (Portugal)

A 100 mm diameter fluid bed has been operated for fast pyrolysis at feed rates of 0.18 to 0.6 kg/h. The maximum total liquid yield at 500°C from pine was 51% which increased to 55% at 600°C. The liquid had characteristics similar to those from other fast pyrolysis systems. Tests have also been carried out on a 300 mm square fluid bed (24). Work is continuing on co-pyrolysis of biomass with plastics (25).

Union Electrica Fenosa (Spain)

Union Fenosa have successfully scaled up the Waterloo fluid bed process to 160 kg/h and this has been operating successfully since September 1993 producing around 400 kg/month (26). Total liquid yields of 55% wt on dry feed at 15% water are being achieved which continues to increase as the liquids recovery section is improved (3). Concepts have been announced for units up to 2 t/h (26)

University of Aston (UK)

An ablative plate pyrolyser has been successful designed, built and operated at capacities up to 3 kg/h giving liquid yields up to 80% wt on dry feed (27). This will be further developed to establish design and performance prediction models as well as producing liquids for testing and chemicals recovery. A small conventional fluid bed has also been commissioned. Work on chemicals extraction and production has recently started including studies on catalytic pyrolysis.

University of Leeds (UK)

Fixed and fluid bed pyrolysis has been carried out on biomass and wastes with catalytic upgrading of the products in the fluid bed work including co-processing with methanol. The fluid bed pyrolysis reactor is externally heated and nitrogen is used as a carrier gas (28). The maximum yield of liquid was 58.8 wt%, obtained at 720°C. Detailed analysis of the liquids by SEC, FTIR have been performed. A dual fluid bed has been used to pyrolyse biomass in an externally heated 75 mm diameter bed, 1 m high with nitrogen as the fluidising gas. Part of the reactor freeboard was packed with ZSM-5 catalyst and a secondary fluid bed has also been used for zeolite upgrading. Liquids were collected before and after pyrolysis for comparison.

University of Sassari (Italy)

Work has been recently carried out on fast pyrolysis of Euphorbia in a 6 g/h externally heated fluid bed microreactor. A maximum total liquid yield of 44 wt% was obtained at 500°C (29).

University of Twente (Netherlands)

An ablative pyrolysis reactor was developed based on particles sliding over a heated rotating cone mixed with heated sand. Total liquid yields of up to 50 wt% were obtained at capacity of 7 kg/h (30). Work is continuing on development of the system to recycle the sand and char in associated fluid beds and a standpipe to provide a continuous system (31). A 50 kg/h unit has been sold to the University of Beijing in China and is due for commissioning early in 1995 (31).

Other

TGA studies are being carried out at the University of Zaragoza, Spain (32) and the Hungarian Academy of Sciences (18); free fall or drop tube experiments at RIT, Sweden (33); modelling studies at the University of Naples, Italy (34); bio-oil analysis studies at the University of Corsica, France (35) and UCL, Belgium (36); wire mesh pyrolysis at Imperial College, London, UK (37); waste wood fast pyrolysis at the Institute of Wood Chemistry, Hamburg, Germany; and waste pyrolysis at low temperature at the University of Cardiff, UK (38).

APPLICATIONS

Although there are several detailed papers in these proceedings, a summary of the opportunities is included which are shown in Figure 1. Within Europe the most promising application is seen as electricity production due to the anticipated ability to use raw bio-oil as produced in an engine or turbine without the need for extensive upgrading as well as the ability to de-couple fuel production from electricity generation with storage and/or transport of the liquid fuel which is not possible for gasifier products and IGCC systems.

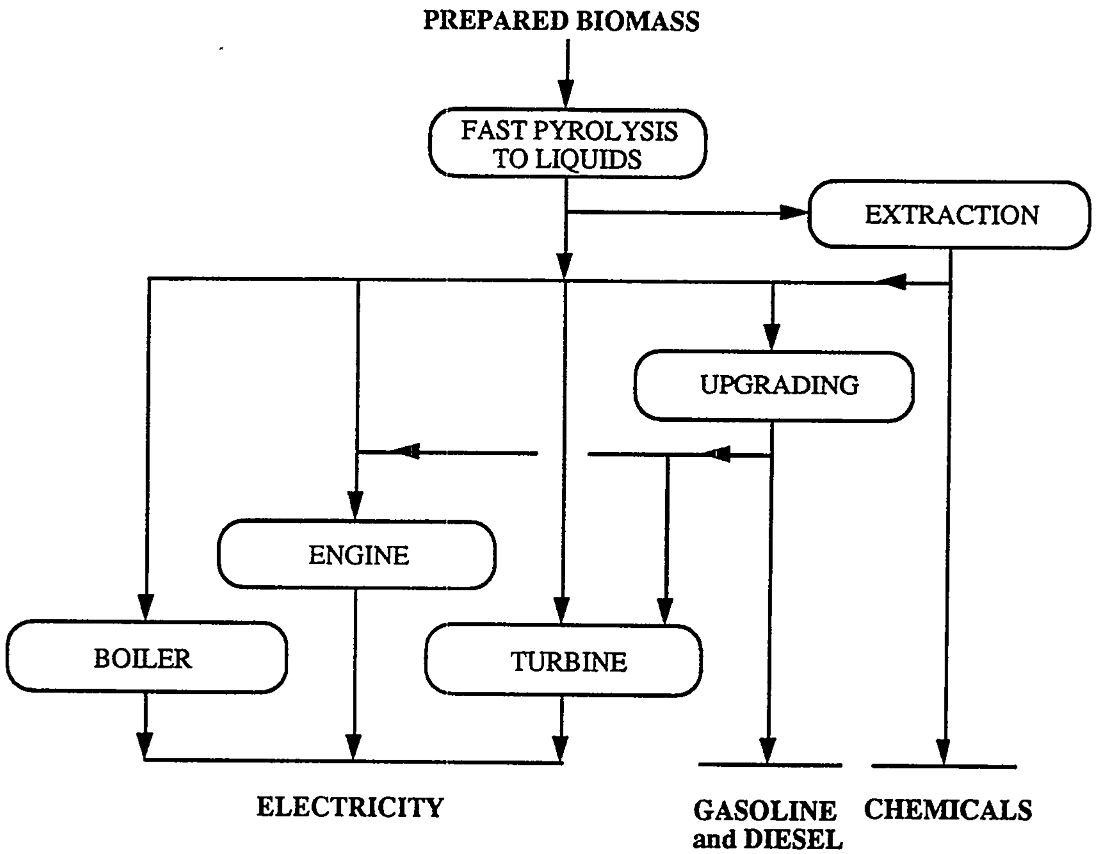

Figure 1 Application of Pyrolysis Liquids

Combustion

Liquid products are easier to handle and transport in combustion applications and this is important in retrofitting existing equipment. Existing oil fired burners cannot be fuelled directly with solid biomass without major reconstruction of the unit, which may not be attractive in uncertain fuel markets, however bio-oils are likely to require only relatively minor modifications of the equipment or even none in some cases. Problems have been reported in handling the fuel with high viscosity and suspended char causing atomisation difficulties and incomplete combustion with some fuels. Now that the problems are recognised, solutions are already being found as reported variously in these proceedings.

Power generation with liquids

A key advantage of production of liquids is that fuel production can be de-coupled from power generation. Peak power provision is thus possible with a much smaller pyrolysis plant, or liquids can be readily transported to a central power plant using engines or turbine. There are additional benefits from potentially higher plant availability from the intermediate fuel storage. The economics of power generation suggest that a niche of up to 10 MWe is available for exploitation which is illustrated later.
Bio-oil has been successfully fired in a diesel test engine, as reported elsewhere in these proceedings, where it behaves very similar to diesel in terms of engine parameters and emissions. A diesel pilot fuel is needed, typically 5% in larger engines, and no significant problems are foreseen in power generation up to 15 MWe per engine. Gas turbine applications are also considered to be feasible although no work has been carried out in the last 10 years nor on fast pyrolysis liquids. However, a new project has recently been implemented to investigate this, which is also reported in these proceedings, and this is more likely to be viable for larger scale applications.

Chemicals

Several hundred chemical constituents have been identified to date, and increasing attention is being paid to recovery of individual compounds or families of chemicals. The potentially much higher value of speciality chemicals compared to fuels could make recovery of even small concentrations viable. An integrated approach to chemicals and fuels production offers interesting possibilities for shorter term economic implementation. Chemicals that have been reported as recovered include polyphenols for resins with formaldehyde, calcium and/or magnesium acetate for biodegradable de-icers, levoglucosan, hydroxyacetaldehyde, and a range of flavourings and essences for the food industry. There are substantial problems to be overcome is establishing markets for the less common chemicals and devising low cost and efficient separation and refining techniques. The only currently viable market opportunity is for speciality food flavourings with a current market size of around US$ 10 million in North America and which could expand to US $ 40 million in 10 years.

ECONOMICS

A key factor in the continuing development of fast pyrolysis processes to eventual commercial implementation is their economic viability. The current main interest in Europe is for electricity generation from biomass with the driving forces of environmental benefits, CO_2 mitigation, socio-economic benefits from re-deployment of surplus agricultural land, and energy independence. These have led to significant fiscal incentives being offered for renewable electricity in many European countries such as prices of up to 20¢/kWh in Italy and up to 14¢/kWh in the UK.

Cost and performance comparison

An indication of the performance and specific capital cost of various thermal conversion to electrical power technologies is summarised in Figures 2 and 3 below which clearly show the potential impact of a successful development of flash pyrolysis and engines on the cost of electricity production.

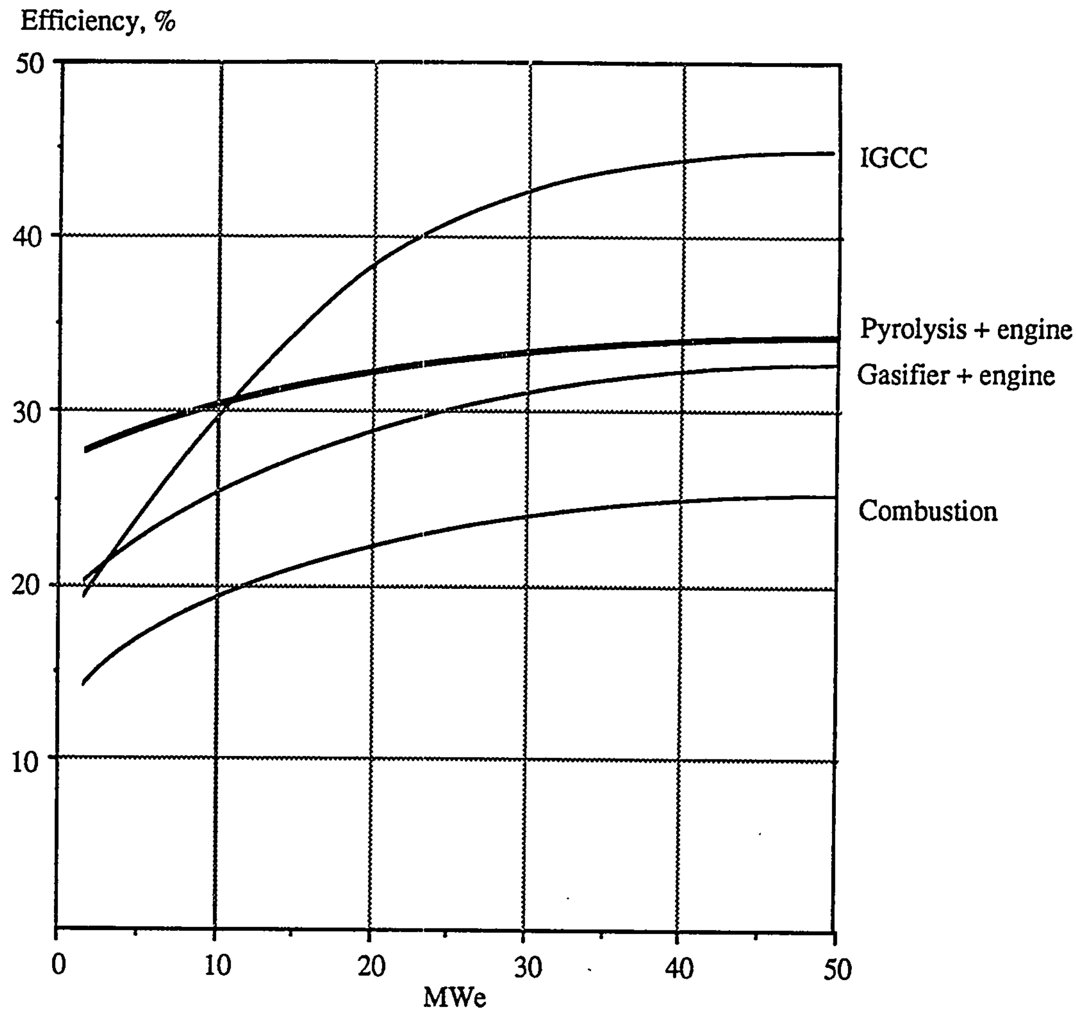

Figure 2 Efficiency vs Size for Power Generation Systems (39)

CONCLUSIONS

Fast pyrolysis is becoming more accepted as an emerging technology with commercial potential for producing high yields of liquid fuels that can be used in many applications as direct substitutes for conventional fuels or as a source of chemicals. There are still problems to be resolved but it is clear that considerable progress is being made in firstly identifying these problems and then finding and defining solutions. There are some interesting challenges to be faced in modifying the fast pyrolysis technology, in upgrading the liquids and adapting applications to accept the unusal behaviour and characteristics of the liquid product. International cooperation is one of the key routes to facilitate such developments and this needs to be encouraged as bioenergy is increasingly accepted as a potentially significant resource. Further research and development of the fundamental science which provides the tools for the design engineer to achieve the performance improvements is also required for successful exploitation.

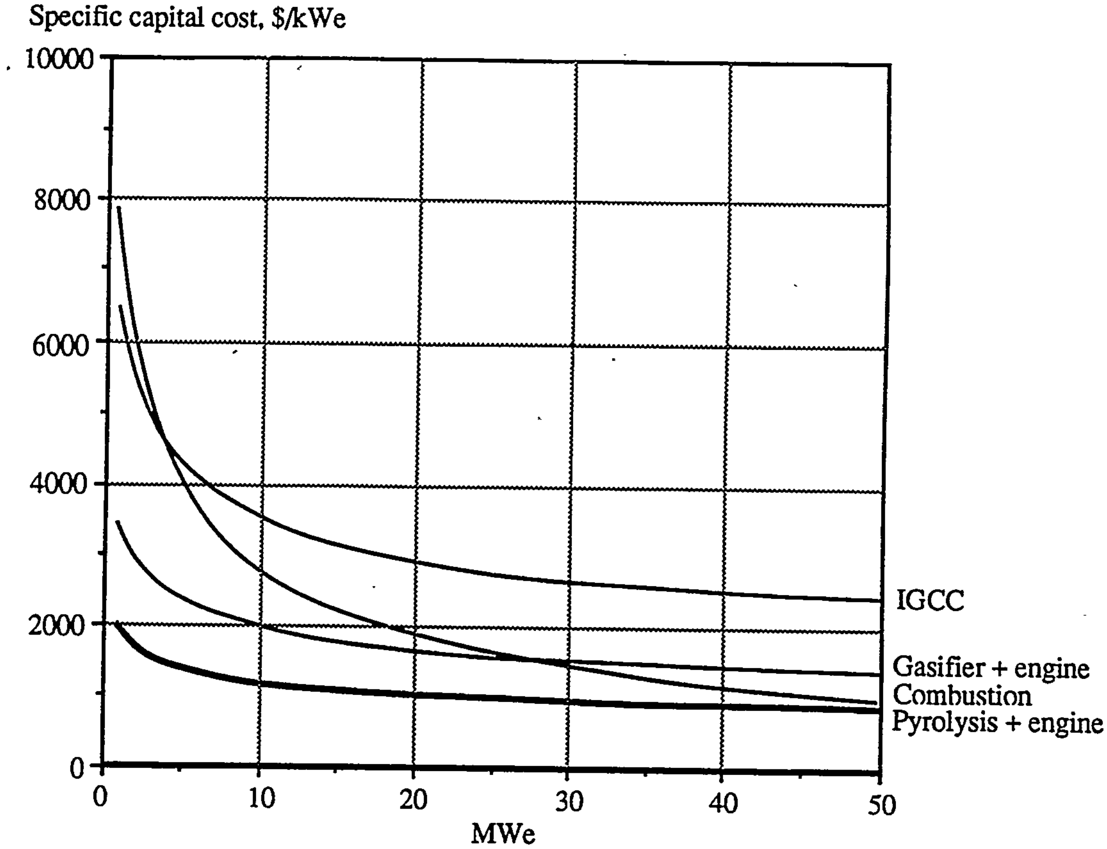

Figure 3 **Specific Capital Cost for Power Generation Systems** (39)

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349

Pyrolysis Oil Economics: Issues and Impacts

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The estimated cost to produce biomass-derived oil (biocrude) ranges from a low of \$17/barrel of oil equivalent (boe) to over \$50/boe. Differences in economic assumptions account for a portion of the variation in estimates, but do not tell the complete story. Process variations, plant size, and feedstock costs are also important cost contributors. In addition, the quality required for specific market applications can significantly affect the cost of the product.

Quantification of the cost elements for the production of biocrude must include factors specific to the feedstock, process, and final market. For a particular system, additional unit operations may be required to meet product specifications. A study was made of the cost contributions of different process sections in an effort to permit design of a facility to meet the needs of a variety of applications. The units may be combined in a number of configurations to provide an indication of the production cost for biocrude.

The biocrude production facility consists of five sections which will be incorporated into a particular process configuration selected from a number of available options. The sections examined in this study include Feed Preparation, Pyrolysis, Solids Removal, Condensation, and Product Treatment/Stabilization. Material and energy balances are calculated using the ASPEN process simulator. Cost figures for the selectable configurations in each section have been developed, and an overall cost of production can be determined for the selected facility.

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BIOPOWER MARKET IMPACT: APPLYING ADVANCED TECHNOLOGIES TO SPECIFIC NEEDS

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ABSTRACT

The impact of biopower on the electric power capacity in the United States is projected to increase 5- to 10-fold by the year 2010. A number of competing technologies will likely be available that will provide a variety of advantages for the U.S. economy, from creating jobs in rural areas to increasing the demand for component manufacturing. Biopower also offers environmental advantages over conventional fossil fuel-fired power plants, particularly global climate change benefits.

Feedstock type and availability, proximity to users or transmission stations, and markets for potential byproducts will influence which biomass conversion technology is selected and the scale of operation. Cofiring biomass in aging coal-fired power plants represents a near-term alternative for reducing sulfur and CO_2 emissions. Producing biocrude from pyrolysis processes may be suitable for isolated feedstock supplies with high transportation costs or to supply fuel to a single large facility in a centralized area. Integrated gasification/combined cycle (IGCC) systems offer high efficiencies and low capital costs. More advanced systems, including fuel cells, will offer additional opportunities for increasing the impact of biopower on the nation's power production.

INTRODUCTION

Biopower systems consist of an entire cycle, from growing and harvesting the biomass resource, to converting and delivering electricity, to recycling carbon dioxide during growth of additional biomass. Biomass feedstock supplies include many types from diverse sources that create technical and economic challenges for biopower plant operators because each feedstock has different physical and thermochemical characteristics and delivered costs. Characteristics of biopower facilities, including feedstock flexibility and capacities that are typically much lower than fossil-fuel power plants, present opportunities for market penetration in nonconventional ways.

Today's biopower industry consists of standalone condensing steam and combined heat and power installations. The overall efficiency of most condensing biopower plants is about 20%, a result of fuel variability and the small scale of units, with the average capacity of current

units at 25 MW_e. Green wood fuels, which constitute a large fraction of biopower feedstock, have about 50% water content; this makes the overall boiler efficiency low compared with fossil fuel power plants.

The U.S. Department of Energy (DOE) projects an increase in biopower generation to 23.5 GW by 2010 (1). As shown in Figure 1, the mix of generating capacity is expected to include: an increasing proportion of integrated gasification combined cycle (IGCC); a steady increase in cofiring, advanced steam cycles, and gas turbine cogeneration; and decreasing contributions from standalone steam cycles and steam turbine cogeneration.

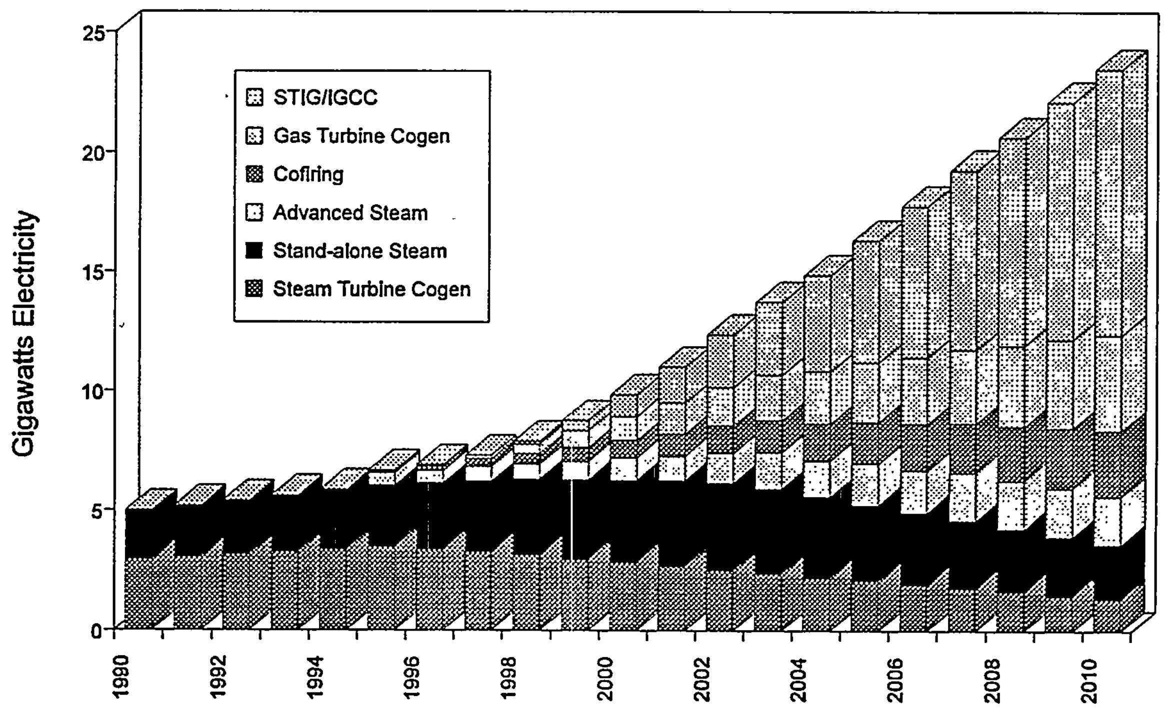

Figure 1. DOE biopower market projections - installed capacity

Several technologies at various stages of deployment are available for biopower generation. In this study, five technologies were examined for use in a variety of market scenarios, from small local generation to large centralized power stations. These technologies are described below, followed by a number of proposed commercialization tracks. Employment and environmental impacts are also discussed.

TECHNOLOGY DESCRIPTIONS

Combustion

Currently, biopower contributes 6.86 gigawatts (GW_e) (2) to the electric power grid in the U.S. Most of this capacity employs relatively inefficient (less than 25% efficiency) direct steam technology. Two common biomass boiler designs are grate combustors (traveling or stationary) and atmospheric circulating fluid bed combustors.

In the grate combustors, fuel feeders evenly distribute the biomass over the grate, which provides a floor on which the fuel can burn. The air chamber located beneath the grate supplies the required air.

Because of the rapid and thorough mixing of inert solids, biomass fuel, and oxygen in a circulating fluidized bed combustor, very high heat transfer rates are obtained. Combustion takes place at lower temperatures than a typical stoker combustor, which offers emission control advantages (particularly thermal NO_x) and reduces the potential for ash agglomeration.

Cofiring

Utility scale pulverized coal (PC) boiler systems can be retrofitted to fire biomass. At low levels (less than 5% heat input), biomass can simply be added to the coal feed system prior to the pulverizers. At higher levels, PC boilers will typically become pulverizer-limited, necessitating the addition of a separate wood feed/comminution system and the substitution of wood firing for coal firing in one row of burners. A number of utility scale PC and cyclone boilers have been tested for biomass cofiring, including TVA's Allen station (a 300 MW cyclone boiler) and Kingston station (a 150 MW T-fired PC) (3).

If the feed/comminution system is not modified, then PC boilers may be adapted for biomass cofiring by adding biomass injection ports, a dump grate, and a biomass combustion air system. Biomass is introduced by feed ports located below the primary coal burners, becomes entrained in the upward flowing gases, and burns in the fireball. Heavier chips that are not entrained in the gas fall to the dump grate where combustion is completed. Because biomass combustion air requirements exceed those of coal, increased fan capacity may be required.

Pyrolysis

Thermal decomposition of biomass in the absence of air results in the production of a liquid product that superficially resembles petroleum. Several reactor designs, including vortex, entrained, and fluid bed reactors, are at various stages of commercialization to produce liquids (4). In each case, the production of biocrude is expected to be decoupled from the production of electricity.

Integrated Gasification/Combined Cycle (IGCC)

Direct-fired and indirect biomass gasifiers have been developed and are being demonstrated to produce power. The Institute of Gas Technology (IGT) has operated a 9-Mgpd direct-fired fluid bed gasification test unit, gasifying a wide variety of biomass. Battelle Columbus Laboratories (BCL) has operated a similarly-sized indirect fast-fluidized gasifier. Additional gasifiers have been designed and operated in the U.S., Europe, and Scandinavia. An excellent review is available (4).

Gasification is a two-step, endothermic process in which a solid fuel is converted into a low- or medium-energy gas. In the first reaction (pyrolysis), the volatile components of the fuel are vaporized by a complex set of reactions. The second reaction (gasification and/or partial combustion) converts the remaining carbon to provide the required heat for the process. Biomass typically contains 2.5 to 3 times more volatile matter than coal; the pyrolysis reaction plays a larger role in biomass gasification.

Close-coupling of the gasification and power systems increases overall conversion efficiency by using both the thermal and chemical energy of hot product gases to fuel the power cycle.

Integrated Gasification/Fuel Cell (IGFC)
Fuel cells are electrochemical devices that convert chemical energy directly into electrical energy, with efficiencies ranging from 50 to 60%. Integrated with a biomass gasifier, the system can produce electricity at extremely high overall efficiencies. Several types of fuel cells are being considered by electric utilities for commercialization. Molten carbonate fuel cells (MCFC) appear to be well-suited to biopower systems because of their flexibility with respect to gas composition. MCFCs can convert CO and methane, as well as hydrogen, thereby using a larger portion of the gasifier output.

APPLICATIONS AND DEVELOPMENT TIMELINES

These five technologies provide an opportunity for increasing the impact of biopower on electricity production in the U.S. Three general areas of market potential include retrofits, distributed or modular plants, and centralized generation facilities. Near-term applications are expected to use waste biomass, with increasing reliance on dedicated feedstocks.

Retrofits of existing coal-fired boilers for biomass fuel offer economic and environmental advantages in the near-term. Significant reduction in greenhouse gases releases can be achieved with relatively small capital investment.

Distributed and modular systems may find a use in isolated regions where transmission lines are inadequate or not available, or where transportation of biomass feedstock to a central processing facility is costly or not feasible.

Centralized generating systems are likely to be larger capacity generating plants with access to feedstock (biomass or biocrude).

A matrix of technology and market applications is given in Table 1.

Table 1. Market applications for biopower technologies.

Technology	Market Application		
	Retrofit	Distributed/Modular	Centralized
Combustion	x		x
Cofire	x		x
Pyrolysis		x	x
IGCC		x	x
IGFC		x	x

Market penetration will depend on the availability of inexpensive feedstocks. The concurrent development of dedicated feedstock supply systems (DFSS) is vital to the expansion of the biopower industry.

Combustion
Of the approximately 1,000 wood-fired plants in operation in the U.S., only one-third offer electricity for sale to the grid. Biomass boilers are in use in the pulp and paper industry as a means to control solid waste and to generate steam and power for in-house energy

requirements. Near-term biopower capacity additions may be expected to rely on this mature technology; no major improvements in production costs are anticipated.

Cofiring

Cofiring biomass in existing utility coal-fired boilers has been proposed and tested as a means to offset sulfur dioxide and fossil fuel-derived carbon dioxide emissions. The advantage of this application is that the modifications to the utility system give a much lower capital investment than building a standalone high efficiency station. If the cofiring is properly engineered, there will be little or no loss in boiler thermal efficiency at biomass cofiring rates of less than 30%. In existing coal-fired installations with individual boilers of 100 to 500 MW_e, up to 20% biomass cofiring would create a significant local market for biomass and would generate a regional biomass feedstock supply infrastructure at the lowest risk.

Pyrolysis

Presently, the NREL experimental ablative fast pyrolysis unit is being scaled up to a 32 megagram per day (Mgpd) unit to produce biocrude. An additional scale-up to 200-300 Mgpd is expected to provide sufficient operating data for additional commercialization decisions.

The University of Waterloo (Canada) has also developed a fast pyrolysis process for producing liquids from biomass. The process has been scaled up by Union Electrica Fenosa in Galacia (northwestern), Spain.

In addition, Ensyn Technologies (Canada) has developed and commercialized an upflow flash pyrolysis reactor, with a number of installations, including Red Arrow Products (Wisconsin) which produces specialty chemicals (flavors) and fuel oil from biomass.

Converting biomass to a liquid provides an opportunity to convert small or disperse amounts, or difficult-to-transport biomass into a useable, transportable fuel for oil-fired turbine generators. Applications include intermediate and peaking power markets.

IGCC

Biomass gasification research continues to address areas of concern, including hot gas cleanup and conditioning, particulate removal, and turbine blade integrity. A major DOE effort is underway to demonstrate biomass gasification. The IGT direct-fired gasifier is being scaled up from 9 Mgpd to 90 Mgpd by the Pacific International Center for High Technology Research (PICHTR) in conjunction with a sugar mill in Hawaii. A 3-5 MW_e gas turbine will be installed for long-duration testing. Research at BCL continues in the area of hot gas conditioning. Joint venture opportunities continue to be pursued by IGT, BCL, and others.

IGFC

Fuel cell developments continue to be monitored. A particular area of concern for fuel cell applications is gas quality. Successes in coal gasification/fuel cell systems are encouraging and interest among utilities remains high. Gas cleanup research currently underway in the IGCC programs is applicable to the fuel cell arena.

ECONOMIC ANALYSIS

Preliminary economics for producing biopower via these five technologies is given in Table 2. These costs represent n^{th} plant costs for mature technologies, and do not represent first generation biopower plant costs for emerging technologies. As there are a large number of

biomass combustion power plants operating today, these costs are representative of current generating costs. Cofiring tests have been performed; estimated costs include credits taken for environmental externalities (CO_2 and SO_2). Pyrolysis, IGCC, and IGFC biopower technologies are developmental; costs are estimates only.

Table 2. Cost of electricity for biopower systems, constant 1990 dollars.

Technology	Power Output (MW)	Efficiency (%)	Capital Cost ($/kW)	Cost of Electricity (¢/kWh)	Ref.
Combustion	20[1] 50[2]	21.6 24.7	1869 1366	7.7 6.4	(5)
Cofire[3]	20[4] 25[5] 38[6]	34.4 36.1 36.1	199-517 203 135	0.5-1.5 0.15 (0.02)	(3)
Pyrolysis	43 110	27.9 33.7	1831 1317	9.8 7.1	(6)
IGCC	60 148	36.7 39.7	1310 1000	6.2 5.0	(7)
IGFC	96	47.0	1100	4.9	(8)

1 California subcritical plant
2 Burlington (VT) subcritical plant
3 Cost of electricity for the cofiring cases are the incremental costs that can be attributed to the biomass
4 15% biomass cofire at the TVA 136 MW Kingston #1 (TN) plant; capital costs range because of feed preparation costs
5 10% biomass cofire at the TVA 251 MW Allen #3 (TN) plant
6 15% biomass cofire at the TVA 251 MW Allen #3 (TN) plant

POTENTIAL ECONOMIC AND ENVIRONMENTAL IMPACTS

The biopower industry in the U.S. will continue to provide a variety of economic and environmental benefits. Establishing DFSS will also provide additional employment to the agricultural sector. The biopower industry offers the prospect of increasing the agricultural sector's income and strengthening regional economic development. Employment opportunities include biomass production, harvesting, transportation, and conversion.

An expanded biopower industry will have a significant impact on the economy, particularly in creating jobs. It is estimated that, by 2010, 284,000 jobs will be attributable to the biopower industry (9), as shown in Figure 2.

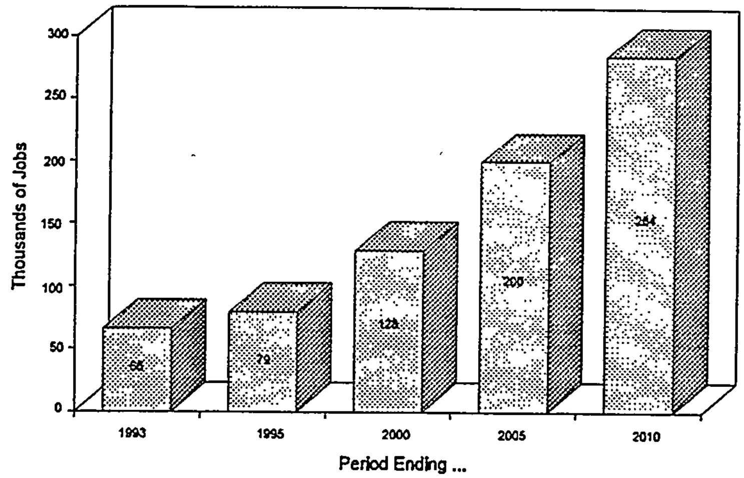

Figure 2. Cumulative Employment Impact of Biopower

Electricity generated from renewable biomass feedstocks offers significant environmental benefits over conventional fossil fuel-derived electricity. Biomass is low in sulfur, typically 0.05 to 0.20 weight percent sulfur. When grown in a sustained manner, the CO_2 released during combustion is fixed by the next generation of feedstock. This provides for a closed CO_2 cycle in the biopower system. Fossil-derived CO_2 continues to contribute to the growing problem of an open greenhouse gas cycle. Environmental impacts, specifically the reduction in CO_2 emissions (9), are shown in Figure 3.

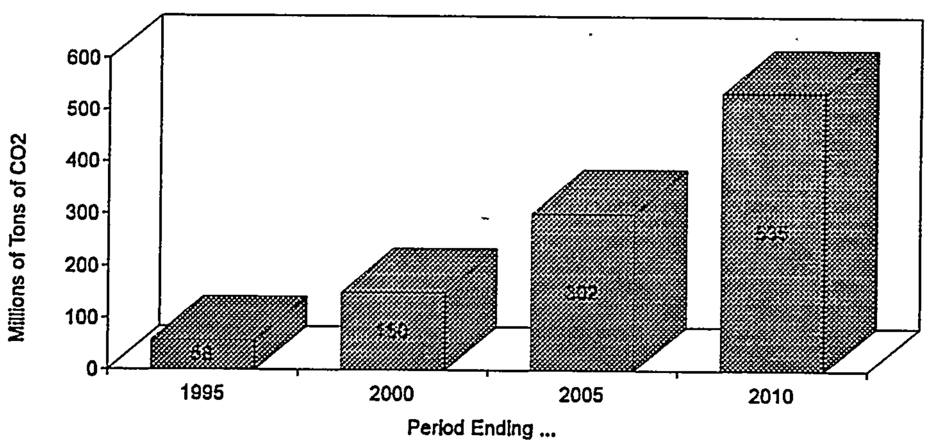

Figure 3. Cumulative Environmental Benefits

CONCLUSIONS

The flexibility of biopower applications with regard to feedstock, technology, capacity, and markets presents an opportunity to provide environmental and employment benefits in the U.S. and abroad. DOE-sponsored research, development, and deployment activities will provide the necessary support for commercialization of economically-viable biopower technologies. Preliminary economic analyses indicate that the five technologies included in this study may be attractive for specific and, in some cases, general applications.

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DESIGN CONCEPT AND HYDRODYNAMICS OF AN AIR-BLOWN CIRCULATING FLUIDISED BED REACTOR FOR BIOMASS FLASH PYROLYSIS

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ABSTRACT

Amongst various thermochemical processes for the exploitation of biomass, flash pyrolysis is known to maximise liquid products yield. Flash pyrolysis is usually carried out in inert gaseous atmospheres, often in entrained or fluidised bed reactor configurations. One of the by-products of flash pyrolysis is char which ideally is utilised to provide the process heat for pyrolysis. A novel reactor configuration has been devised to utilise this energy by recycling the char to the lower zone of circulating fluid bed (CFB) reactor which is modified by the addition of a bubbling fluid bed where the char is burned in air. The heat released to the product gases and sand provides the thermal energy to carry out the biomass devolatilisation in the CFB riser. This paper summarises the reactor concept and design considerations as well as providing experimental data derived from a full scale cold model of the CFB which was constructed and operated in order to determine the hydrodynamic behaviour of the reactor.

INTRODUCTION

Low grade fuels such as biomass, RDF and solid wastes play an increasingly important role in the energy scene. In particular, biomass is readily recognised as the only renewable alternative fuel, its utilisation for energy purposes being realised by direct use, as in combustion, or by upgrading into a more valuable and usable product or fuel. This upgrading may be by physical, biological, chemical or thermal methods to give a solid fuel (e.g. char), liquid fuel (e.g. ethanol, methanol or bio-oil) or gaseous fuel (e.g. biogas, low or medium energy gas).

Of the available biomass conversion options, pyrolysis processes that maximise liquid (bio-oil) yield are of particular interest, since liquid products are easier to handle in subsequent utilisation schemes and are better for retrofitting existing equipment. The characteristics of pyrolysis processes for liquids production are high heat supply rate, rapid heating rate, moderate reactor temperatures and short gas/vapour product residence times. All of these requirements may be readily achieved in entrained or fluidised bed reactor configurations.

An interesting option for biomass flash pyrolysis which satisfies the basic requirements set out above is a modified circulating fluidised bed - an entrained flow reactor with recovery and recirculation of entrained and captured solids. This type of reactor can also lead to improved energy integration by utilising the energy content of the char product, which is recirculated with the inert heat carrier material to the bottom of the bed where it is

combusted, with biomass injected in the upper section of the bed to be entrained in the hot combustion products. The design concept as well as experimental data for the complex hydrodynamics of this system are described below.

FLASH PYROLYSIS PROCESSES

Flash pyrolysis is known to give high yields of pyrolysis liquid (or bio-fuel-oil) of up to 75 wt% from wood and 80 wt % from cellulose on a dry ash free (d.a.f.) feed basis. In order to achieve these high yields, high heating rates (>1000°C/s) combined with moderate reactor temperatures (<625°C), short gas/vapour residence times (<2 s) and rapid quenching of the vapour phase organic compounds are required. Several reviews of pyrolysis technologies have recently been published (1, 2).

In order to avoid slow pyrolysis conditions which favour char and secondary tar formation reactions, most flash pyrolysis processes utilise high heating rates. To achieve this, flash pyrolysis technologies have used principally three methods of heat transfer:

- gas phase heat transfer from hot gases to the biomass,
- gas-solid phase heat transfer from hot gases to inert solids to the biomass,
- heat transfer through a hot solid surface (i.e. ablative pyrolysis which, however, is not discussed further here).

The first method of heat transfer is used in entrained flow reactor configurations. Wood particles (<2mm) are carried co-currently by hot combustion products or inert gases, provided by stoichiometric combustion of a fuel gas (usually propane) with air, into an up-flow tube, where they are rapidly heated and pyrolysed (1-2s). Entrained-flow pyrolysis has been researched extensively in the U.S.A. by Knight et al. since the 1970s and their process has undergone a series of modifications with results indicating liquid yields approaching 60 wt.% (3, 4). Recently, Egemin NV, a Belgian firm, have operated an entrained flow reactor, where hot carrier gases are tangentially mixed with biomass (~5mm) in the reactor entrance, the swirl created to improve mixing and heat transfer (5). Maximum liquid yields of 55 wt% were achieved due to incomplete pyrolysis and loss of liquids from the recovery system.

The second method of heat transfer is readily found in fluidised bed reactor types. The development of a bench scale unit fluidised bed unit followed by the design of a larger process unit by researchers at the University of Waterloo (UW), Canada, led to liquid yields of up to 80 wt% for a wood feed (6). The main features of the UW process is the operation of the fluidised bed in the "blow-through" method, in which the fluidising gas velocity is controlled so that only product char is entrained from the reactor, while the inert bed material remains in the reactor.

The most critical feature in the case of the UW flash pyrolysis process is the method of heat transfer used and the subsequent constraints this imposes on reactor design. Since heat is mainly transferred to biomass particles by the incoming fluidising gas, large gas flows are required to sustain the pyrolysis reaction, which in turn leads to a large fluidised bed area in order to maintain low gas/vapour product residence times. The large bed area requirement may impose limitations on the scale up size of this reactor, a matter which has been discussed in a recent technoeconomic assessment of biomass liquefaction processes (7).

To meet the high heat transfer rates required and short gas/vapour product residence time, the University of Western Ontario (UWO), Canada developed a rapid pyrolysis process termed ultrapyrolysis. A transported bed reactor uses hot solids to transfer heat to biomass particles. Development and scale-up was continued by Ensyn Engineering Associates Inc., a Canadian firm incorporated in 1984, and resulted in the Rapid Thermal Processing (RTP)

reactors. Three different RTP reactor system configurations are currently active, each system incorporating recirculating, transported-bed designs, which achieve rapid heat transfer in a turbulent mixing zone (8).

The RTP-1 design is a downflow configuration, in which the feedstock (biomass) and heat carrier (sand) move downwards, while the heat carrier is flowing upwards in a transfer line. The RTP-2 and RTP-3 designs are upflow systems, where the feed and heat carrier flow upwards in a transfer line. The common denominator of each system is rapid mixing, resulting in rapid heat transfer and allowing precise control of gas/vapour product residence times.

THE CONCEPT OF A CFB AIR-BLOWN PYROLYSER

All flash pyrolysis processes discussed here are carried out in a range of reactor configurations but they all use an inert atmosphere in the reactor provided by nitrogen recycle gas (6, 8) or flue gases produced by stoichiometric propane combustion (3, 5, 6). The advantage of such an approach is that there is no free oxygen so that organic vapours produced during biomass pyrolysis are not oxidised. On the other hand, these processes can result in scale-up problems related to the need for the supply of a very large quantity of hot gas to provide the energy required, which in turn can lead to longer contact times and/or larger reactor volumes. There is also the potential problem of recycle gas clean-up to avoid deposition of oil and tar in the recycle compressor. In a commercial process, the char produced will have to be burned to provide heat for the pyrolysis reaction and/or biomass pretreatment system (e.g. drying) and to minimise char storage and handling problems.

The heat required for the pyrolysis reactions may be supplied by inert particles as a circulating heat carrier which pass through a combustion system where they are heated by combustion of char and returned to the pyrolyser. The utilisation of the char energy content has been given much attention giving rise to a range of configurations. Figure 1 is a basic schematic of a typical char utilisation system. Biomass is fed into a pyrolysis reactor where it contacts hot inert sand giving rapid heat transfer leading to high volatiles yields from pyrolysis. The pyrolysis products and entrained solids pass to the solids recovery system, typically a cyclone, where sand and char are removed. The solids are then fed with air to a combustion zone, where combustion takes place to provide the energy needed for the pyrolysis reactions. This energy is transferred to the pyrolysis reactor by sand circulation system between the two reactors.

A comparison between a dual fluidised bed system and a single one is shown in Figures 1 and 2. Relevant examples of the twin fluidised bed system configuration, Figure 1, include the Battelle RDF gasification system which utilising two physically separate reactors - one for the gasification and one for the combustion of derived char to provide heat to carry out the gasification process (9); and the Italenergie/AGIP S.p.A. biomass gasification system, which utilises the twin fluid-bed principle (10). A paper, recently presented by ENEL (11), suggests that the Ensyn pyrolysis reactor is based on a circulating or transported bed with solids recirculation.

A simpler solution to the twin fluid bed system would be to utilise char in the same reactor, a feature that reduces complexity and the related equipment cost. In a single fluidised bed reactor system, Figure 2, this can be achieved by returning char to the bottom of the reactor just above the distributor, and restricting the fluidising gas flow rate to that necessary to carry out stoichiometric char combustion to avoid oxygen breakthrough to the pyrolysis zone above. The return of char to the bottom of the reactor is accomplished by recirculating the entire char-sand mixture after separation from the product gas and vapours.

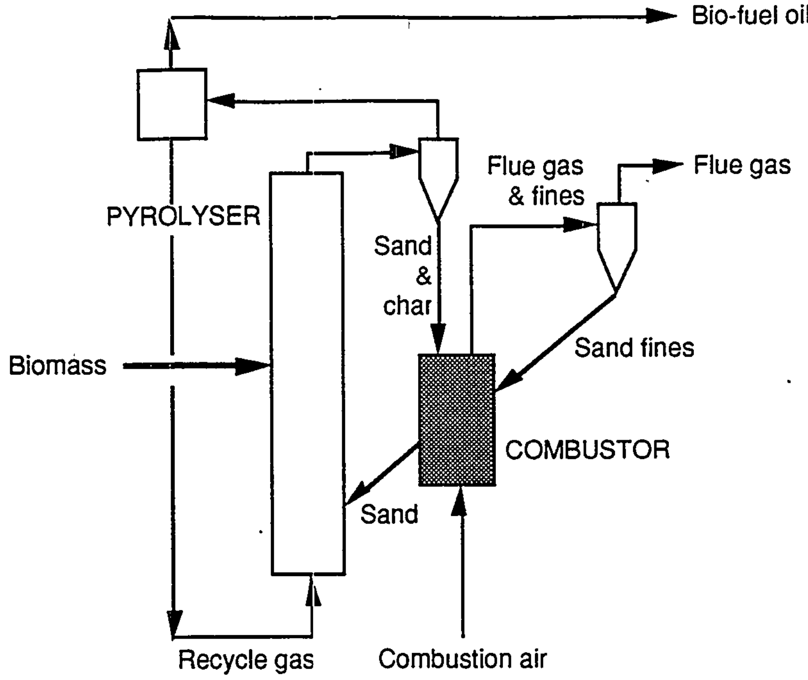

Figure 1: The Twin Fluid Bed System Configuration

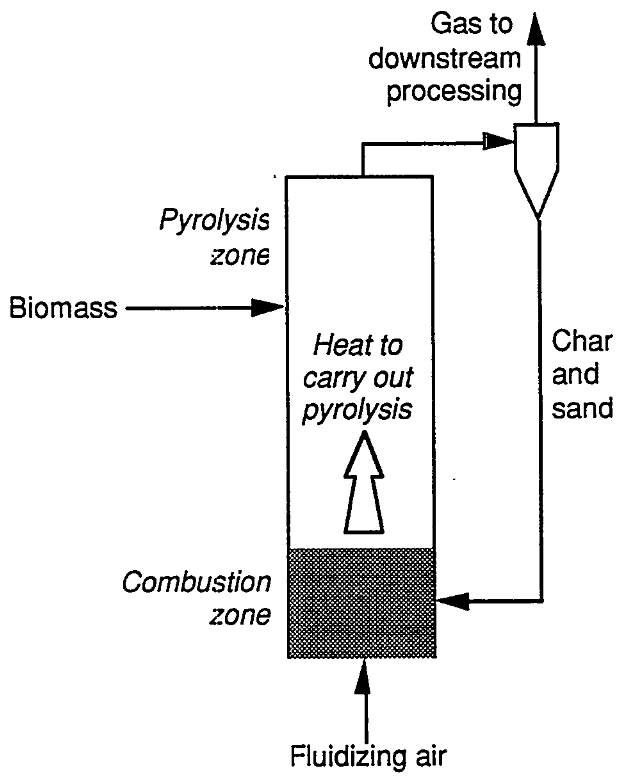

Figure 2: The Single Fluid Bed System Configurations

ENGINEERING DESIGN

The reactor to achieve such a solids flow pattern is based on a Circulating Fluidised Bed (CFB) where solids are entrained in a vertical tubular reactor (riser) to carry out the pyrolysis reaction followed by solids separation in several cyclones in series. The gas and vapours pass to the liquid collection system. The separated sand and char is recycled down a riser, the flow rate of which is controlled by a non-mechanical valve - an "L" valve. The sand and char are returned to the base of the CFB which is modified as a bubbling fluid bed combuster where the char is burned in a stoichiometric flow of air to reheat the sand and provide a hot gas flow to entrain the reheated sand up the riser to continue the pyrolysis process. The main constituents of the system described above are shown in Figure 3.

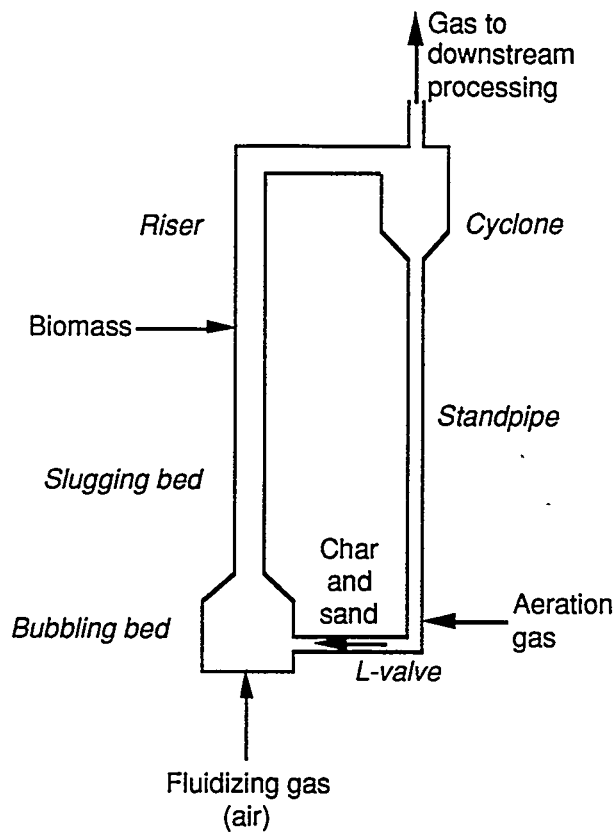

Figure 3 : CFB reactor main components

Due to slugging in the riser section, the sand entrainment rate is quite high resulting in the establishment of fast bed mode conditions in the riser section, characterised by the formation of many agglomerates (strands or clusters) of refluxing particles, which continuously coalesce and reform. Each cluster is assumed to behave like a single larger particle, in a time mean sense, which gives the fast bed a number of potential advantages:

(i) The ability to maintain relatively dense beds of fine particles at high velocities, allowing high throughput in small cross-section units.

(ii) Intense backmixing of solids promoting temperature uniformity.

(iii) The "effective agglomerates" formed are in no sense close packed, allowing substantial convective through flow, while the surface area of each individual particle remains active.

(iv) Although the solids entrainment rate is high, the CFB is not an entrained reactor in the sense that the gas velocity is similar to the solids velocity and no internal circulation is possible. In a CFB reactor, the external circulation (via the riser - cyclone - standpipe - valve system) is accompanied by an internal recirculation of solids in the riser due to the constantly changing densely packed strands and clusters, a recirculation that leads to enhanced heat and mass transfer coefficients.

(v) Since the CFB is a transport reactor, its structure is characterised not only by gas velocity and solid properties, but also by the Solids Circulation Rate (SCR), a parameter easily adjustable and associated with the ability to rapidly change the riser inventory, a feature giving potential control advantages to any circulating system.

These characteristics indicate that the CFB air blown pyrolyser should be an effective system for biomass flash pyrolysis.

CFB HYDRODYNAMICS-EFFECT ON REACTOR PERFORMANCE

The continuous circulation of hot solids in a reactor system as described above can effectively transport heat from one part of the system to the other. The rate of biomass to bio-oil conversion is related to the magnitude of the heat transfer coefficient which determines the heat flux to the biomass particles and this is dependent upon the Solids Circulation Rate (SCR). It can, therefore, be claimed that a higher SCR, resulting in a denser riser, will promote a higher heat transfer coefficient, which will subsequently promote higher biomass to oil conversion rates. The dependence of heat transfer coefficient upon solids hold-up has already been shown in CFB boilers to follow an approximately linear function between measured heat transfer coefficients and suspension density (12).

CFBs can be conveniently grouped into two types, constant and variable inventory units, terms corresponding to units in which SCRs are uncontrolled and controlled respectively. In a Constant-Inventory-CFB (CICFB), the total amount of solids in the riser is more or less fixed, since the solids recycle system is not designed to accommodate a varying solids load; while in a Variable-Inventory-CFB (VICFB), the SCR is controlled by a solids storage device (e.g. a hopper or an accompanying fluidised bed) in the recycle loop (13).

The density profile along the riser in a variable inventory unit may be continuously varied over much wider ranges than in a constant inventory one (due to increased storage capacity of the solids recycle loop and the proper adjustment of the SCR through the re-injection system). Thus a variable inventory CFB should be more suited to this reactor configuration, since it becomes much more flexible by operating in different modes. This unit also has the advantage that the limited gas quantity injected to the non-mechanical valve used to aerate and control the solids back to char combustion chamber, is easily controlled in the downstream equipment used for the recovery of the organic vapours.

COLD MODEL PERFORMANCE

Preliminary mass and energy balance calculations, based on the final product distribution from a well assessed flash pyrolysis process in a fluidised bed reactor and assuming a 10 kg/h biomass feedrate, have indicated the following dimensions for the CFB reactor which are summarised in Table 1 (6, 14, 15). Furthermore, a heat balance, assuming the energy requirements limited to heat for raising the temperature to reaction temperature and heat of vaporisation of products, taken over the riser section indicates a 10:1 heat carrier to biomass mass ratio, which agrees exactly the values calculated by other researchers (16), values that are easily obtained in CFB reactor as will be further depicted.

Table 1: CFB reactor design parameters

	Parameters	Cold model	Hot unit
Bubbling bed			
Bed temperature	T_B, (°C)	20	800
Gas density	ρ_g, (kg/m^3)	1.293	0.329
Gas velocity	u_B, (m/s)	0.35	0.35
Bed diameter	D_B, (m)	0.17	0.20
Circulating bed			
Bed temperature	T_R, (°C)	20	500
Gas density	ρ_g, (kg/m^3)	1.293	0.457
Gas velocityt	u_R, (m/s)	4.0	4.0
Reactor diameter	D_R, (m)	0.05	0.05
Gas flow rate	G_{gas}^{in}, (kg/h)	36.55	12.92

The cold model unit, constructed specifically for the study of macroscopic scale gas-solids interaction phenomena is shown in Figure 4 and is described in detail elsewhere (17).

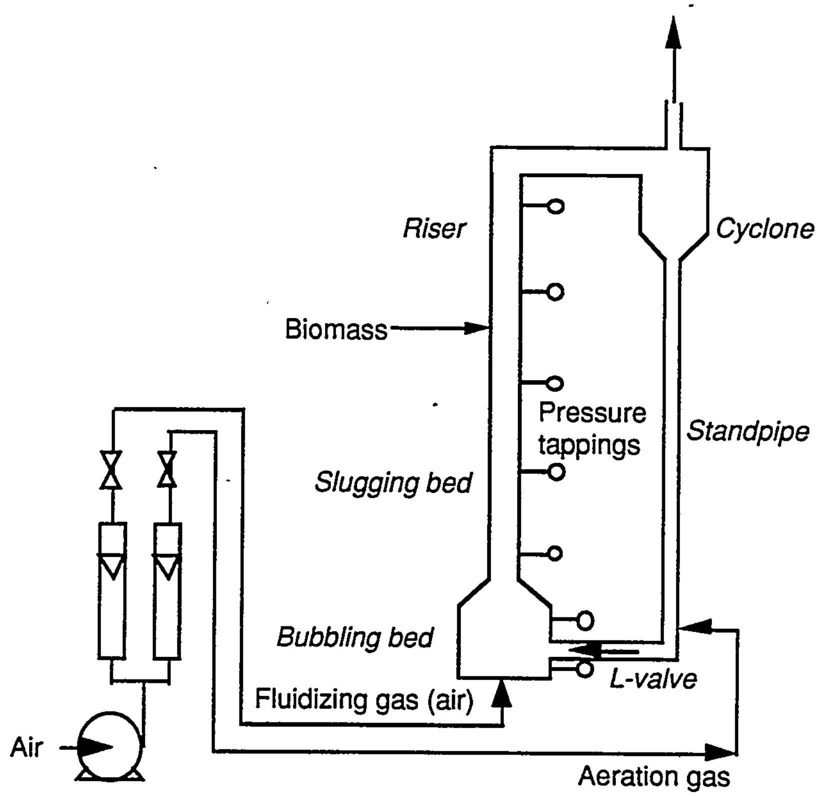

Figure 4: The CFB Cold Model

Pressure profiles were determined, allowing the average bed voidage (and hence the average Suspension Solids Density (SSD) ρ_{susp}, in the riser section to be calculated. The assumption made is that the pressure measured is due primarily to the static head of solids in the suspension, the contribution of gas-wall friction, solids-wall friction and solids acceleration being negligible (18, 19), i.e.:

$$\Delta P=(\rho_s-\rho_g)*g*(1-\hat{A})*z \quad [1]$$

where:

ΔP	pressure drop (Pa)
ρ_s	solids density (kg/m^3)
ρ_g	gas density (kg/Nm^3)
g	acceleration due to gravity (m/s^2)
$\hat{A}$	voidage
z	height (m)

The suspension density, is directly correlated to the voidage by the following relationship:

$$\rho_{susp} = (1-\hat{A}_{avg})*(\rho_s-\rho_g) \quad [2]$$

where:

ρ_{susp}	suspension density (kg/m^3)

The suspension density (solids hold-up) is determined for the riser section, and as a consequence the average riser voidage is shown to be a function of three process variables, referred to below:

- initial bed inventory (IBI)
- fluidising gas flow (FGF)
- aeration gas flow (AGF)

With the two first process variables pre-set (FGF is directly correlated to biomass input, while the IBI is fixed for each run) the only operating variable is the AGF, which determines suspension density and consequently regulates the extent of pyrolysis reaction by changing the heat transfer coefficient to the biomass.

The average riser voidage is derived, considering the riser pressure drop, from equation [1]. Subsequently, the average suspension density in the riser may be derived applying equation [2]. The results are presented in Figure 5, clearly indicating that a denser suspension, (lower average riser voidage) and hence a higher heat transfer rate, can be achieved for higher total solids charging (IBI) at the same air velocity (FGF).

To determine the effect of AGF upon SCR at actual experimental conditions, experiments were carried out for fixed FGF and IBI, while only varying AGF. These experiments indicate that minimum AGF adjustments have a pronounced effect in SCR, allowing for significant adjusting measures (denser or leaner suspensions respectively) during pyrolysis. Due to the reservoir of solids in the lower portion of the CFB reactor, the system becomes much more flexible in that it can operate with a constant gas flow rate (and thus a constant vapour residence time), while varying the solids throughput which influences SCR. These results are shown in Figure 6. The SCR was measured using the solids diversion technique in the standpipe section (18).

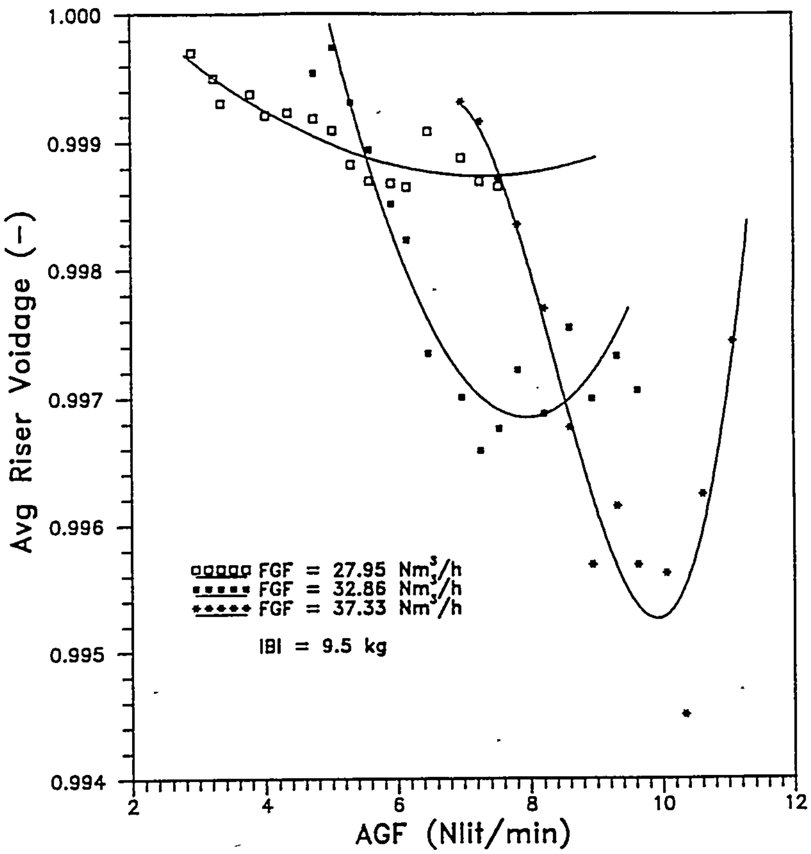

Figure 5: Average riser voidage dependence on AGF for varying fluidising gas flowrates (IBI =9.5 kg)

Standpipe stability is a very important parameter for the reliable operation and stability of the system and was studied extensively by cold model experiments. Solids circulation between the different subsystems of the CFB reactor depends decisively on a good design of the solids reinjection system and smooth operation. This subsystem is made of standpipe and a non-mechanical valve (L-valve) and serves three important functions:

i to transfer solids from a region of lower to higher pressure,
ii to provide a seal against gas flow in an undesirable direction,
iii to regulate the solids circulation rate.

For gas not to short-circuit up the standpipe, a dense down flowing suspension is required. This is achieved by in a moving-bed flow or a fluidised-bed flow mode, operated at nearly minimum fluidising conditions. Coarse sand particles are usually made to move down vertical pipes slowly and in moving bed flow. In this type of flow, the movement of gas relative to solids, characterised by the slip velocity, u_{sl}, is kept lower than that of the solids moving at minimum fluidisation velocity, u_{mf}. This mode of operation, i.e. solids downflow in the moving-bed regime, keeps the voidage in the standpipe as low as possible allowing a maximum pressure build-up and adequate movement of solids.

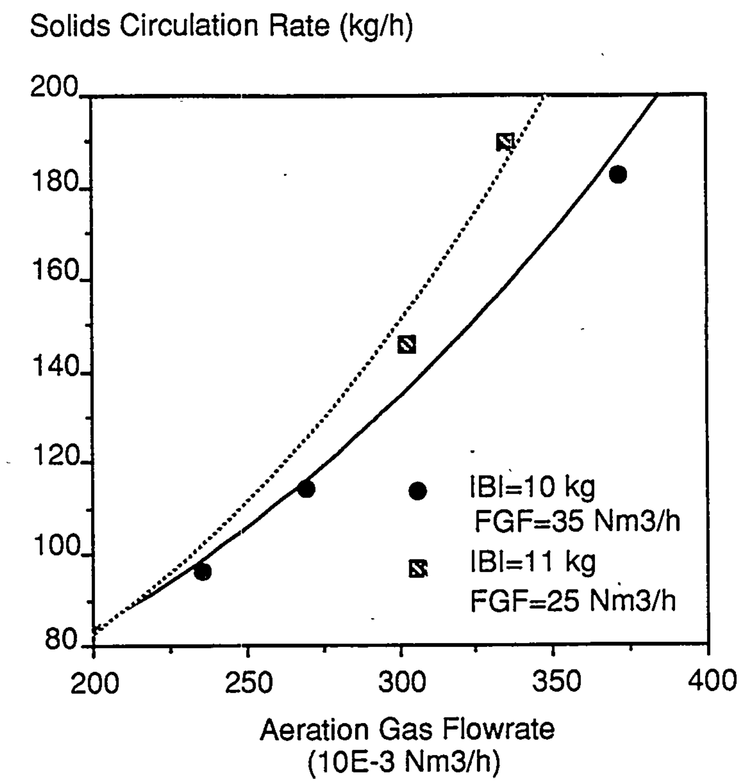

Figure 6: Solids Circulation Rates vs AGF for sets of FGF and IBI

Stable standpipe operation is achieved by maintaining the pressure gradient in the standpipe below the fluidised bed density. The fluidised bed density is obtained by gradually raising AGF, and equals to the weight of the solids per unit area when the particles become fluidised (20). Standpipe gradient profile and the average riser voidage plotted vs AGF for given fluidising gas flowrates and initial bed inventories are shown in Figure 7. The decline observed, and hence a marked loss in the ability of the system to effectively transport solids in a steady mode, is due to the transition from moving-bed to fluidised bed flow mode in the standpipe. This results in turn in a lean standpipe, occupied by solids plugs and slugs and hence to a leaner riser (increase of average riser voidage) which has a deleterious effect on heat transfer. Care should therefore be taken to maintain stabile operation of the system since standpipe flow mode transitions directly affect heat transfer and hence biomass devolatilisation.

HOT UNIT EXPERIMENTS

The design characteristics of the system have been thoroughly analysed elsewhere (21), where a detailed analysis of the downstream processing, namely a shell-and-tube heat exchanger, and the biomass feeding system, namely a twin screw feeder, is given.

A summary of hot unit runs is given in Table 2 which shows one of the major problems is the inadequacy of downstream liquid collection equipment. The heat exchanger was able to remove the heat from the gaseous stream. However, indirect cooling of pyrolytic vapours is not a suitable method, problems with tube exchanger plugging already reported by Scott and Piskorz.

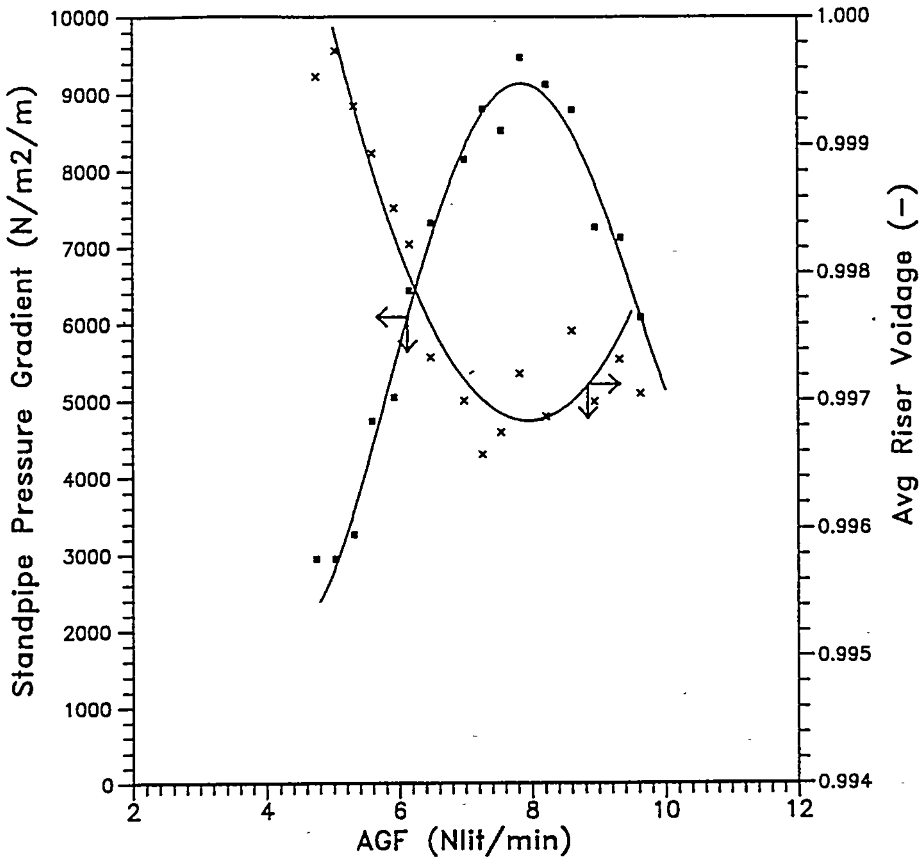

Figure 7: Standpipe Pressure Gradient and Average Riser Voidage vs AGF.

The main problem with indirect cooling is the mechanism of heat transfer itself. A significant temperature gradient exists in the heat exchanger tube wall, so that the heavy fraction is condensed at the walls and flows slowly downwards, significantly decreasing the effective tube area and thus preventing free gas passage flow. Char and sand particles escaping the solids recovery system (cyclones) then deposit on the thick condensate film further reducing the free tube area. This eventually blocks the heat exchanger causing cessation of the experiment.

A brief discussion on the results shown in Table 2 follows:

- continuous feeding was applied in run R1 at a lower biomass feeding rate than that specified for pyrolysis. As a consequence the high air/biomass ratio promoted oxidation and gasification reactions in the riser resulting in high temperature and low yields of a brownish liquid with a low density.
- intermittent feeding was applied in runs R2, R3 and R4. The product char was smoothly recirculated within the loop, which was shown by a gradual increase in combuster temperature from char oxidation, a decrease in riser temperature, higher yields of liquid and an increased liquid density. The higher yields of liquid fraction in runs R3 and R4 are due to the addition of a small heat exchanger (run R3) and a liquid trap (run R4).

Table 2: Summary of hot unit pyrolysis runs

Run No	Biomass fed (kg/h) #	Reactor ¶ temperature, °C	Liquid fraction recovered (%wt, dry feed)	Density of liquid fraction (5) (kg/m3)
R1	4.0	700-750	30%	0.99
R2	2.3	550	45%	1.07
R3	1.8	525	50%	1.08
R4	2.5	480	55%	1.08

\# Calculated from, feeder calibration curve and measured feeding time (moisture content ~8%)

¶ Measured above biomass feeding point

The reduced temperatures in the riser section in Runs R2-R4, result in reactions favouring volatiles formation, while the explanation for the somewhat lower than expected density values are due to the fact that, as explained above, the heavier bio-oil components are mainly retained in the heat exchanger. As a result, this also affects the calorific value of the liquid recovered, which for runs R2, R3 and R4 ranges between 11.8-13.5 MJ/kg. Analyses of the liquids have not yet been carried out.

Some problems are also associated with the internal char utilisation including:

- efficiency of the solids recovery systems, which proved very effective for the inert heat carrier (sand) but not for char particles, which frequently escaped in the downstream processing contributing to heat exchanger fouling
- production of a fragile char residue which results in the generation of high percentage of fines which are difficult to recover in the solids recovery system, and which are rapidly elutriated during the combustion process.

Finally, an important consideration is that the system design must provide sufficient time for complete char oxidation in the combuster and satisfactory utilisation of the incoming oxidant air. This is achieved by correct sizing the combustion chamber based on the following assumptions:

- the combustion is isothermal
- all oxygen should form CO_2 with the char
- char combustion is diffusion/reaction controlled
- char combustion proceeds through a modified "single-film" mechanism, in which oxidation occurs first by diffusion of oxygen to the carbon surface, reaction with solid carbon to form CO and second by diffusion of CO to the emulsion phase in which is oxidised to CO_2
- the gas is assumed to flow without dispersion in both the bubbles and the emulsion phase
- a simplified two-phase model (Kunii-Levenspiel) describing the interaction between emulsion and bubble phase was used.

Preliminary results indicate that the concentration of oxygen in the emulsion phase reduces very quickly to zero (approximately 10% of bed height), while the oxygen concentration of the particulate phase reduces more slowly approximately 25-30% of bed height). The products of combustion are then CO2 approximately 90-95%) and CO approximately 5-10%). However, these results need to be demonstrated.

CONCLUSIONS

A novel reactor for flash pyrolysis of biomass has been designed and a cold model for studying the hydrodynamics of the proposed system was constructed and tested. This modified circulating fluidised bed, modified by the addition of a bubbling bed at the bottom of the riser, operates at relatively high velocities and utilises the energy content of by-product char by combusting it in the bubbling bed in the lower reaction zone, while hot sand is circulating throughout the system as an inert heat carrier material.

Cold model operation indicates that the CFB hydrodynamics and stability favour pyrolysis, while the process parameters can be easily adjusted to match the required high heat and mass transfer rates.

Modifications to the hot unit resulted from cold model experiments. These include oversizing the first cyclone to accommodate the increased solids loading of the gas stream as well as the addition of a secondary cyclone, to allow fine sand and char capture. The aeration gas supply to the non-mechanical valve was modified to improve control. Preliminary hot unit experiments have revealed that as far as temperature uniformity and heat transfer requirements are concerned, the objectives of the system have been met. A significant feature of the design is the high thermal efficiency resulting from internally utilising the energy content of by-product char.

The main problems yet to be overcome remain:

- optimisation of the solids recovery system
- derivation of reliable experimental data concerning char combustion in order to verify and modify the model used for combuster sizing
- effect of char fragmentation on system performance
- development of diagnostic methods for determination of solids circulation rates in the hot unit
- improvement of the gas-cooling system and liquids collection system.

ACKNOWLEDGEMENTS

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THE PRODUCTION AND HANDLING OF WFPP BIO-OIL AND ITS IMPLICATIONS FOR COMBUSTION

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ABSTRACT

Union Fenosa has been operating and improving a pilot plant for the thermochemical conversion of biomass based on the Waterloo Flash Pyrolysis Process (WFPP) for some time. Valuable experience has been accumulated regarding the influence of the different parameters that can affect the production of the bio-oil. Bio-oil with relatively stable characteristics, in respect to physical and thermal aspects, has been achieved and is regularly produced. Work underway will clarify the influence on the bio-oil characteristics of some different feedstocks, or modification of reaction parameters, as well as stability and reliability of the operation, thermal and energy balances, and techno-economic assessment.

Some experiments in combustion, of limited consistency, were carried out in the past in collaboration with the Universidad Politécnica de Madrid. New programs to further explore this aspect are underway.

INTRODUCTION

A pilot plant for converting biomass into alternative bio-fuels through a flash pyrolysis process was constructed and commissioned in the Galicia region in northwestern Spain. The area is a heavily forested area, with large biomass resources. They have been estimated at more than 4 million tons per year (2), the main species being *Eucalyptus*, *Pinus* and *Ulex*. The construction of the plant was financially supported by the Commission of the European Union (DGXII), the Spanish Electric Research Programme (PIE) and Union Fenosa.

The plant was started in mid-1992, although the first year was basically devoted to testing the components and start up trials. During the past year, the plant has been producing significant quantities of bio-oil. By implementing several minor modifications into the initial design, we have a more stable operation and therefore a bio-oil of better characteristics in respect to their physical and thermal properties.

The purpose of this paper is to review some of our experience acquired during the operation of the plant, especially looking at the influence of the production step on the combustion of pyrolysis oils.

THE UNION FENOSA WFPP PYROLYSIS PLANT

The plant is based on the Waterloo Flash Pyrolysis Process (Table 1). It has a nominal capacity of approximately 8.5 t/day (360 kg/h) of raw biomass of 5 t/day (200 kg/h) of dry biomass in continuous operation. Forest residues are dried and ground before being introduced into a fluidized bed reactor where pyrolysis occurs. To this effect, the Union Fenosa plant has a preparation unit in which the biomass is

ground up to a maximum size of approximately 3 mm and dried to 8%-10% moisture content. Larger particles could result in incomplete pyrolysis of the chips. Higher moisture content increases the water content of the resulting liquid product.

Once prepared, the biomass is introduced into a fluidized bed reactor where the biomass mixes with a hot gas that fluidizes the bed and makes up the necessary heat for the pyrolysis reaction. Maximum yields of the pyrolysis reaction occur at about 500°C with residence times in the range of 0.5 to 1 s. The resulting products are separated and cooled yielding a liquid fraction (Pyrolysis bio-oil) and charcoal. The non-condensable gases are recirculated to the reactor once they are preheated. No refrigeration is required in the process as only ambient water is used in some of the components to control temperature. A more detailed description of the plant has been previously reported (4) (5).

Table. 1 - Basic process data of the Union Fenosa WFPP Pyrolysis plant.

Raw material	- Chipped biomass, mainly forest residues and energy crops - Moisture content: 30% - 45%
Capacity	- 200 kg/h of dry biomass of 300-360 kg/h of raw biomass (according to moisture content)
Process	- Flash Pyrolysis in a fluid bed reactor, vertical up-flow, low pressure, non oxidizing atmosphere, sand bed and recirculation of gases - Temperature: 500°C - Pressure: 50 kPa - Residence time: 0.5-1 s
Product yields (as produced)	- Bio-oil 130-150 kg/h (65% to 75% wt) - Bio-charcoal 20-30 kg/h (10% to 15% wt) - Non condensable gas (10% to 18% wt)

During the first period of operation of the plant the effort has concentrated in the production of bio-oil from eucalyptus chips. As mentioned before, eucalyptus is an important resource available in the area and is suitable as a feedstock for the process, according to laboratory tests. Minor trials with variable success have been conducted with other biomass types.

Most of the problems encountered while operating the plant were related to feeding the biomass and circulating the bio-oil and other secondary aspects and not to the pyrolysis process itself. We found that discontinuing operation with occasional stops and start-ups is a major problem in pyrolysis plants as in other thermal-chemical processes. Interruptions result in sudden changes in the process conditions (pressures and temperatures) producing troubles in the circulation of the oil along the separation system.

Spraying or washing with recirculated oil is necessary in critical points of the system. However, the flow, temperature and disposition of the injections should be carefully implemented. Excessive recirculation of the product, often together with sudden heatings, results in significant changes in its properties.

On the other hand, the time required for stabilizing the process is considerably longer than in bench scale units. Therefore, there are limitations on the evaluation of the influence of process parameters on the product quality and characteristics.

BIO-OIL CHARACTERISTICS

The characteristics of the bio-oil produced in the plant has been progressively improved in respect to the critical parameters such as water content, microcarbon percentage, etc. The more stabilized process is

allowing a more uniform product from run to run. Table 2 shows the typical range of analyses of bio-oil obtained at the plant. No post-production treatment has been used.

Table 2. Analysis of bio-oils of the Union Fenosa WFPP Pyrolysis plant

Water	15 - 25	%
PH	1.95 - 2.60	
Microcarbon (1.6 μm)	0.5 - 0.8	%
Ash	0.01 - 0.14	%
Density	1.21 - 1.26	gr/cm^3
Viscosity at 25°C	400 - 1200	cp
Viscosity at 50°C	55 - 150	cp
Volatiles (105°C)	26 - 35	%
Water insolubles	25 - 30	%
HHV	16.5 - 17.6	MJ/kg

Note: Data compiled from analysis carried out be independent laboratories such as Université Catholique du Louvain, ENEL, VTT, Universidad de Santiago and University of Waterloo.
The percentages refer to the total weight of the sample.

IMPLICATION OF PRODUCTION ASPECTS ON BIO-OIL CHARACTERISTICS

Very few combustion experiments have been carried out with pyrolysis oils. Consequently the knowledge about the influence of bio-oil characteristics in the combustion process is very limited. Most of the problems encountered so far refer to the previous step of injection rather than to the combustion itself. Pyrolysis oils of low water content, appropriate density and high BTU have been attributed as difficult to burn when the real problem was the injection of the fuel, prefiltering, feeding of the nozzles, etc.

A number of chemical and physical properties are expected to influence this process. For instance: water content, quantity of solids or microcarbon, viscosity, heating value, etc.

Water content:

The water content of the bio-oil has a direct influence in the performance of pyrolysis oils in combustion by influencing the HHV, the viscosity, etc. During the production step in the plant there are a number of factors conditioning this parameter: the nature of the biomass used, its moisture content, the parameters controlling the pyrolysis reactions, etc.

Water contents between 15% and 25% in weight are regularly achieved in our plant. Even when the lower values seem to be more desirable because of the expected increase in calorific value, there is some limitation imposed by the parallel increase in viscosity that could cause problems for the handling and injection of the fuel. On the other hand, for big installations the cost of drying the biomass prior to the pyrolysis should be explored and compared with the improvement on the quality of the oil.

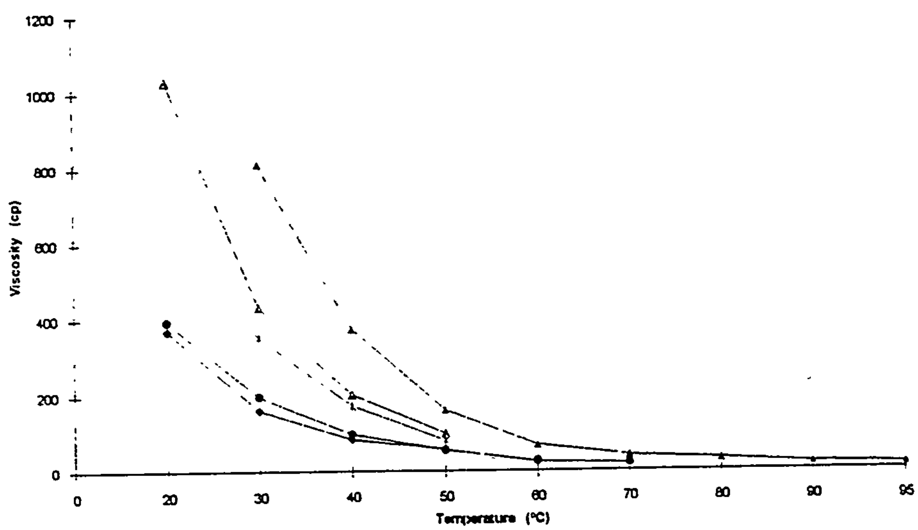
Microcarbon or solids content:

The quantity of solid particles of the so call "microcarbon" is a critical characteristic of the bio-oil in regard to the injection step. A number of filtration systems have been attempted to reduce this content from pyrolysis oil samples with different success. Values below 0.8% in weight are regularly obtained in our plant. An appropriate system of collecting the solid fraction is the key for these results. Char is not fluidized and its removal is achieved in a cyclone, i.e., transport mode. This results in little attrition and therefore in an oil product with low char content.

An effort should be made to standardize the term "microcarbon" as different laboratories are using different analytical methods and filter sizes to estimate this value. For instance, we found that for one of our bio-oils the microcarbon percentage is reduced from 0.8% to 0.54% in weight when a glass filter of 8.0 μm is used instead of the 1.6 μm. This is specially important when comparing different bio-oils.

Viscosity:

The viscosity influences the method of injection of the oil for its combustion, the election between atmospheric or pressurize atomizing, the need of preheating, etc. Heating the bio-oil can reduce the viscosity to an appropriate value. Figure 1 shows the variation with temperature of a number of bio-oils produced in our plant (3).



<u>SOURCE</u>: Université Catholique du Louvain (3).

<u>Figure 1</u>-. Variation with temperature of the viscosity of four Union Fenosa WFPP bio-oils.

<u>SOURCE</u>: Université Catholique du Louvain (3)

Figure 1. Variation with temperature of the viscosity of four Union Fenosa WFPP bio-oils

However, the effect of high temperature on pyrolysis oil can significantly transform its characteristics as these liquids have proven to be quite thermally unstable. Severe heating for extended periods can result in polymerization of the aldehydes and other components. The *Université Catholique du Louvain* recently noted that the viscosity of one of our bio-oil samples at 25°C rose to 3710 cp, from the original viscosity at 25°C of 1106 cp, after being heated at 95°C (3). At the *Università degli Studi di Sassari* studies of the thermal stability of pyrolysis oils have been conducted by keeping sealed vessels at 100°C for several hours. The viscosity was measured after cooling to 20°C showing an increase in the viscosity as the time of exposure to high temperatures increased (1).

Therefore, heating at very high temperatures should be done only if essential, and in any case, immediately before injection.

Heating value:

Bio-oil of 16.5 to 17.5 MJ/kg HHV as is (not on a dry basis) is regularly obtained in the plant. The calorific value of the oil is related to the water content in some degree, although this correlation is not clearly understood. On the other hand, it seems that the volatile content of the oil closely affects its heating value and this volatile content changes according to the pyrolysis process used in its production.

Feedstock nature:

Eucalyptus is an unusual wood from the chemical point of view, quite different from northern hardwoods such as poplar. For example, the eucalyptus bio-oils always have considerably higher sugar content than poplar oils. This sugar content can potentially cause problems in spraying the bio-oil through a nozzle if its nature is not taken into account when choosing the injection equipment and parameters.

CONCLUSIONS

It is desirable that the present effort on combustion tests of pyrolysis oil should help to define the minimum quality standard required to achieve proper combustion of the oil. These efforts should clarify the parameters of major influence on the process, and address pyrolysis plant optimization to produce the most suitable bio-oils. As a result of the studies, it would be possible to conclude whether, or in which circumstances, direct combustion of pyrolysis oils is an attractive alternative technically and economically, or in which scenarios it is necessary to develop a more sophisticated fuel by upgrading the crude bio-oil by catalytic hydrotreating, zeolite synthesis or other alternatives.

A standardization of the analytical methods used in pyrolysis oil analysis is required to validate experiments carried out by different organizations. Combustion tests carried out with pyrolysis oils produced with different biomass types should be contrasted cautiously due to the inherent characteristics of each product. We expect that bio-oils produced from different biomass will require specific equipment and parameters to achieve successful injection and combustion.

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Environmental Considerations in the Production and Use of Biomass Fast Pyrolysis Oils.

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This paper will review the state of environmental regulations as they relate to the utilization of fast pyrolysis oils from biomass. Properties of the oils and components in the oils which are impacted by the regulations will be identified. Toxicological test results will be mentioned only as they impact on regulations. Potential environmental regulatory roadblocks will be discussed. Emphasis will be on U.S. federal regulations, which will be presented. The effects of state and local implementation of the regulations will be considered. Comparison to regulations in other countries will also be attempted.

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ASSESSMENT OF REGULATORY REQUIREMENTS FOR PROCESS EFFLUENTS FROM THERMOCHEMICAL BIOMASS CONVERSION

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ABBREVIATIONS LIST

BAT	-	best available technology
BDAT	-	best demonstrated available technology
CA	-	California
CAA	-	Clean Air Act
CEQ	-	Council of Environmental Quality
CFR	-	Code of Federal Regulations
Ci	-	curie
CWA		Clean Water Act
DCG		derived concentration guide
DOE		United States Department of Energy
EA		environmental assessment
EIS		environmental impact assessement
EPA		United States Environmental Protection Agency
FONSI		finding of no significant impact
HW		hazardous waste
ICRP		International Council on Radiation Protection
L		liter
LDR		Land Disposal Restrictions
MCL		maximum contaminant level
NA		not available
NAAQS		National Ambient Air Quality Standards
NEPA		National Environmental Policy Act
NREL		National Renewable Energy Laboratory
POTW		publicly owned treatment works
RCRA		Resource Conservation and Recovery Act
SDWA		Safe Drinking Water Act
SMCL		secondary maximum contaminant level
TSD		treatment storage and disposal facility
TT		treatment technique requirement in effect

CONTENTS

TABLES

CHARTS

1.0 INTRODUCTION

The report includes a listing of potential hazardous process effluent components from thermochemical biomass conversion and reviews the extent that these materials are regulated. The review of regulations is an extensive coverage of all federal regulations and Department of Energy (DOE) directives important to the operation and activities of a biomass comversion facility located at a DOE site. The components considered are those identified in earlier studies of biomass conversion effluents [Elliott 1992, Fagernas 1992].

In general, the statutes and regulations discussed in this report protect human health and the environment by regulating discharges to the air, groundwater, surface water, and soil. To do so, the regulations contain performance and design standards and criteria that must be met by plant operators. Permits may also be required; these permits prescribe the specific performance, design and siting criteria that must be met to satisfy the regulatory standards. Some permits authorize direct discharges of substances to the environment. In other cases, additional permits are required before waste management and other facilities are allowed to operate. The permits for a facility may be issued by several regulatory agencies, such as the United States Environmental Protection Agency (EPA), state departments of ecology or social and health services, or local agencies, such as county health districts, city sewer systems, or pollution control authorities.

Any DOE biomass conversion operation is subject to DOE orders that cover waste management and disposal, and protection of workers, the public, and the environment. For the most part, the DOE orders add procedural requirements, but the 5400.5 order described in this report specifies actual effluent limits. In the case of biomass, the limits specified are expected to be well above the effluent amounts.

The multiple levels of governmental involvement derive from the high level of public interest in environmental regulation. State regulatory agencies often play major roles in implementing and enforcing environmental laws. A number of the federal environmental statutes provide for a dual federal-state regulatory program where the states are given the opportunity to enact and enforce laws. While these laws must meet congressionally mandated minimum criteria, states are generally free to adopt and enforce even <u>more stringent</u> environmental requirements. In states that have been delegated and accepted responsibility for enforcing various federal environmental laws [such for the Resource Conservation and Recovery Act (RCRA)], the state becomes the primary permitting and enforcement mechanism. All of these regulations are subject to continual updating, which usually tightens the restrictions. Therefore, the specific site of any biomass conversion operation will determine the exact level of pollution control required, and may be different from a similar operation in another location.

It is important to note that the release specifications described below apply to both normal operations and off-normal operations. That is, releases of any type over the set limits

can result in fines and other legal retribution, whether the releases were purposeful or accidental. Therefore, plant design should take into account releases of all types. Maintenance procedures as well, especially equipment cleanout, needs to be considered in the plant design. Allowance must be made for collection of all waste streams from the plant, including off-spec startup products, spent maintenance materials, and feedstock storage pile runoff.

2.0 APPLICABLE FEDERAL STATUTES AND REGULATORY ISSUES

2.1 THE NATIONAL ENVIRONMENTAL POLICY ACT OF 1969, 42 USC 4321 et seq.

The National Environmental Policy Act (NEPA) is often called the "cornerstone" of national environmental policy. It established the tone for future environmental legislation. When NEPA was passed in 1969, it established a national environmental policy that ensures full consideration of the potential environmental impacts of major federal activities in the decision-making process. Section 2 of the Act states that the role of NEPA is to establish an environmental policy and "to promote efforts which will prevent or eliminate damage to the environment and biosphere and stimulate the health and welfare of man; to enrich the understanding of the ecological systems and natural resources important to the nation." It is included in this discussion, not because it contains specific discharge limits itself, but because it will apply (to varying extent) to any decision to build or locate a treatment facility at a DOE site.

Section 102(2)(C) is the primary governing provision of NEPA. It states that all agencies of the Federal Government shall review proposed major Federal actions to determine whether they may have a significant effect upon the environment. For those actions that have the potential for significant environmental effects, an environmental impact statement (EIS) must be prepared.

Once an agency has identified a proposed action it must gather the data necessary to determine whether that action is a major federal action that could significantly affect the quality of the human environment [NEPA Section 102(2)(C)]. Council of Environmental Quality (CEQ) implementing regulations define "human environment" to include the natural and physical environment and the relationship of people to the environment. When answering this question, agencies have traditionally developed several supporting documents. These documents are not specifically required by the statute.

If uncertainty exists in the "level of impact" of the proposed action, an Environmental Assessment (EA) must be completed. CEQ created the EA as a means of gathering sufficient data to determine whether an EIS is necessary. According to CEQ regulations, the EA must include the need for the proposed action, alternatives to the proposed action, the environmental impacts of the action and its alternatives, and a listing of agencies and persons consulted.

Upon examination of the EA, if it is determined that the action will not have a significant impact on the environment a "Finding of No Significant Impact" (FONSI) is prepared. The FONSI must include the EA or a summary of the EA (40 CFR 1508.13).

If an action is determined to be "major" and its impact on the environment could be significant, an Environmental Impact Statement is completed. The EIS is the foundation of NEPA, and is the document required by Section 102(2)(C). The purpose of

the EIS is to provide decision makers with the information they need to make sound, environmental decisions, and to inform the public and provide them with an opportunity to participate in the process.

The environmental consequences section of the EIS contains a scientific analysis of the direct and indirect environmental effects of the proposed action and alternatives (46 FR 18026, 1981, Q.7). The narrative must include a discussion of the proposed action's direct effects and their significance, the proposed action's indirect effects and their significance, and the environmental effects of each alternative.

Following the description of the alternative actions and their environmental impact, an environmentally preferable alternative is identified. The environmentally preferable alternative is usually the one that causes the least damage to the biological and physical environment, and that also best protects and preserves historic, cultural, and natural resources (46 FR 18026, 1981, Q. 6a). The environmentally preferred alternative is not necessarily the alternative chosen in the final "Record of Decision." The comparison of alternatives must be done in a consistent manner that allows each alternative to be "fairly" compared with each other.

A draft EIS is published in the Federal Register to request and receive pubic comment. In response to the comments, DOE may need to conduct further research including additional target ecological risk assessments. Some comments may not be incorported into the final EIS. If a comment is <u>not</u>

incorporated, an explanation should be prepared as to why the comment did not warrant further response on the part of the agency (40 CFR 1503.4). At this point the final EIS is published and a final preferred alternative is stated. NEPA does not require that the most environmentally preferred alternative be chosen, but rather that environmental consequences be accounted for in the decision-making process. A Record of Decision is then published.

Despite its 20 years of existence, the language within NEPA remains vague and often results in confusion about how to meet regulatory requirements. Case law continues to lead to new interpretation. Of the issues that have repeatedly arisen as a result of vague language, the decision on the threshold determination (Section 102(2)), is the most critical and difficult to resolve.

2.2 THE RESOURCE CONSERVATION AND RECOVERY ACT, 42 USC 6901 et seq.

The Resource Conservation and Recovery Act was enacted by Congress to establish a "cradle to grave" system to control the generation treatment, storage, and/or dispose of hazardous waste. Through the provisions of RCRA and subsequent amendments, Congress required the EPA to promulgate an expansive body of regulations which would protect "human health and the environment." EPA's implementing regulations define solid and hazardous waste, establish standards and requires a manifest system for hazardous waste generators and transporters, establish

standards and permit provisions for facilities that treat, store, and/or dispose of hazardous waste, and establish requirements for state delegation of RCRA implementation authority. As stated earlier, many states have been delegated implementation authority and have adopted even more stringent requirements. RCRA also requires facility owners to carry out corrective actions for releases of hazardous substances.

RCRA in divided into ten subtitles, the most significant being Subtitle C, which establishes the hazardous waste management program. EPA's RCRA implementation regulations appear in 40 CFR 260-268 and 270-272. Generators of hazardous waste have the responsibility to determine whether their wastes are hazardous, notify EPA that they are managing a hazardous waste, obtain an EPA identification number for the generating facility and verify that transportation, treatment, storage, and disposal of the waste is conducted only by those who have obtained EPA numbers. The generators must also prepare a Uniform Hazardous Waste Manifest to track waste to ensure that hazardous waste actually reaches its destination.

RCRA requires every owner or operator of a treatment, storage and/or disposal (TSD) facility to obtain a permit. (Section 3005). Permit applications must show the facility will be in compliance with TSD standards. These standards cover such topics as waste analysis, security, inspections, local standards and compliance with the manifest system. (40 CFR Parts 264 and 265). Permit applications will be issued by states authorized under RCRA and by the EPA regional administrator in other states. Some general ongoing requirements for operation and monitoring of

a RCRA facility include the maintenance of records for all hazardous wastes handled by the facility, reporting, monitoring, inspection, and compliance with the manifest system, contingency plans, maintenance and operation of the facility, and compliance with RCRA Section 3005 relating to permits.

The RCRA regulatory standards that have been promulgated pursuant to RCRA and that are of interest to DOE are found in 40 CFR 261, Regulations for identifying Hazardous Waste; 40 CFR 264/265, Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities; and 40 CFR 268, Land Disposal Restrictions (LDR).

2.2.1 Identification of Hazardous Waste

The EPA is required by RCRA to regulate hazardous wastes which pose a danger to the environment or to public health. The land disposal restrictions are one of the vehicles used by the EPA to protect the environment and public health from hazardous waste. In order to implement the requirements imposed upon them by RCRA the EPA had to further define "hazardous waste." The EPA has adopted a two fold approach to defining hazardous waste. The EPA has specifically listed certain wastes as hazardous and identified four "hazardous characteristics" which make a waste hazardous if one or more of them apply.

Listed hazardous wastes are wastes that the EPA has specifically identified as being hazardous. A complete listing of hazardous wastes can be found in 20 CFR Part 261. The EPA has divided the listed hazardous wastes into three subcategories:

- hazardous waste from non-specific sources
- hazardous waste from specific sources
- acute hazardous wastes or toxic waste discarded from commercial chemical products, off-specification species, container residues, and spill residues

Each listed hazardous waste is assigned an EPA Hazardous Waste Code number. These codes are used to identify the specific hazardous waste constituents. The codes are then assigned a specific treatment technology or a maximum constituent concentration level. Chart 1 contains the three categories of listed wastes, the applicable CFR section, and the range of hazardous waste codes assigned to the particular group.

Chart 1. Listed Hazardous Waste EPA Codes

Listed Hazardous Waste Subcategory	CFR Section	EPA Code #'s
Hazardous waste from non-specific sources	20 CFR 261.31	F001 -- FXXX
Hazardous waste from specific sources	20 CFR 261.32	K001 -- KXXX
Acute hazardous waste from discarded commercial chemical products, off spec. species, & container/spill residues.	20 CFR 261.33(e)	P001 -- PXXX
Toxic waste from discarded commercial chem. products, off spec. species & container/spill residues.	20 CFR 261.33(f)	U001 -- UXXX

In addition to the listed hazardous wastes, the EPA has also designated any solid waste that exhibits one or more of certain defined hazardous characteristics as a hazardous waste. These hazardous characteristics are grouped into four subcategories; 1) ignitability, 2) corrosivity, 3) reactivity, and 4) toxicity. Chart 2 shows the EPA's hazardous waste code number assigned to each of these characteristics, the CFR code section which discusses it, and the actual characteristic.

Chart 2. Characteristic Hazardous Waste EPA Codes

Waste Code #	**CFR # (20 CFR 261)**	**Characteristic**	**Description of Substance**
D001	261.21(a)(1)	Ignitability	Liquid, other than aqueous solution containing < 24% alcohol by volume and has a flash pt < 60 degrees C.
D001	261.21(a)(2)	Ignitability	Not a liquid & is capable under standard temperature & pressure of causing fire through friction absorption of moisture or spontaneous chem. changes and, when ignited, burs so vigorously & persistently that creates a hazard
D001	261.21(a)(3)	Ignitability	Ignitable compressed gas (49 CFR 173.3)
D001	261.21(a)(4)	Ignitability	Oxidizer (49 CFR 173.151)

D002	261.22(a)(1)	Corrosivity	Aqueous & pH less <=2 or >=12.5
D002	261.22(a)(2)	Corrosivity	Liquid which corrodes steel (SAE 1020) at a rate > 6.35 mm/yr @ a temp of 55 degrees C.
D003	261.23(a)(1)	Reactivity	Normally unstable & readily undergoes violent change w/0 detonating
D003	261.23(a)(2)	Reactivity	Reacts violently with water
D003	261.23(a)(3)	Reactivity	Forms potentially explosive mixtures with water
D003	261.23(a)(4)	Reactivity	When mixed with water, it generates toxic gases, vapors or fumes in dangerous quantity
D003	261.23(a)(5)	Reactivity	It is cyanide or sulfide bearing waste which when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors or fumes in dangerous quantities.
D003	261.23(a)(6)	Reactivity	Capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement
D003	261.23(a)(7)	Reactivity	Readily capable of decomposition or reaction at standard temperature & pressure

D003	261.23(a)(8)	Reactivity	It is a forbidden explosive as defined in 49 CFR 173.51; or a Class A or B explosive.
D004-DXXX	261.24 Tbl 1	Toxicity	The EPA has assigned this range of numbers to wastes that exhibit the toxicity characteristic. The CFR cite specifically describes the numerous substances which are considered toxic.

2.2.2 Treatment Standards

40 CFR 268 prohibits land disposal of certain hazardous waste. RCRA required the EPA to establish treatment standards for each restricted hazardous waste to allow for disposal. The EPA based these treatment standards upon the performance of the best demonstrated available technology (BDAT) to treat the waste. The EPA used the various BDATs to establish treatment standards as either specific technologies or as maximum constituent concentration levels. If a specific technology is expressed as the treatment standard, that technology must be used. If the standard is expressed only as a concentration level, the regulated community may use any technology not otherwise disapproved by the EPA. For example, it is impermissible to merely dilute a waste to meet a concentration level.

Hazardous waste code numbers are used to identify and assign the required treatment standard(s). The EPA has expressed the treatment standards in essentially three different manners.

- Treatment standards expressed as waste extract constituent concentrations (Table CCWE).
- Treatment standards expressed as specified technologies. (Table 2 & 3)
- Treatment standards expressed as waste concentrations (Table CCW).

It is not uncommon for a particular hazardous waste to carry more than one waste code. The EPA requires these wastes be treated with the applicable treatment standard for each waste code. For example, if a waste is assigned both a D001 and D002 waste code (i.e. ignitable and corrosive hazardous waste characteristics), the waste must meet the treatment standard applicable for both D001 and D002 wastes. This applies to both characteristic hazardous waste and to the listed hazardous waste. However, if a listed hazardous waste exhibits one or more hazardous characteristics and the characteristic constituent or property is specifically addressed in the treatment standard for the listed waste, only that treatment is required.

2.2.3 Hazardous Chemicals

Commercial chemical products, manufacturing chemical intermediates, off-speciation commercial chemical products, or manufactured chemical intermediates, per 40 CFR 261.33, are identified as either acute hazardous wastes and assigned a P001-P123 EPA hazardous waste number or toxic wastes and assigned a U001-U243 EPA hazardous waste code.

2.3 CLEAN WATER ACT, 33 USC 1251 et seq.

The basic regulatory framework for water pollution control was established by the adoption of the Federal Water Pollution Control Act (FWPCA) in 1972. This act has been amended several times (most recently in 1987) and was renamed the CWA in 1977. Section 101 of the CWA describes its purpose as "to restore and maintain the chemical, physical, and biological integrity of the Nation's waters." The requirements under the CWA are directed at uniform discharge standards from both existing and new sources even if the discharges do not result in violation of water quality standards.

The current form of the CWA contains five elements upon from which it attempts to achieve its objective:

1) minimum effluent standards for each industry,
2) water quality standards,
3) a discharge permit program,
4) toxic chemical and oil spill provisions, and
5) a revolving construction loan program for publicly owned treatment works (POTWs).

The discharge of "pollutants" from a point source must be in compliance with a National Pollutant Discharge Elimination System (NPDES) permit. Pollutants under the CWA include biological oxygen demand, suspended solids, fecal coliform bacteria, and pH. Discharges not from a point source or those from dredge/fill activities (Section 404) or discharges to a POTW are regulated under different sections of the CWA.

The NPDES permit for point source discharges can be issued by the EPA or the state. The EPA has based its permit requirements upon two general sets of standards: categorical standards and water quality criteria. Application of the appropriate standards can often depend upon the state's classification of the water receiving the discharge.

Categorical standards are technology-based standards that are applicable to various categories of industrial discharges. These standards are based upon and in reference to pollution control technology. Standards vary depending upon the nature of the point source and the type of pollutant being discharged. (40 CFR Parts 304, 405-471)

Section 304(a)(1) of the CWA [33 USC 1314(a)(1)] requires the EPA to publish ambient water quality criteria or standards. These standards will include a designated use or uses for a particular body of water and water quality criteria will be assigned based upon these uses. The criteria are not rules and do not in themselves have regulatory impact. However, they do present scientific data on the effects of various contaminants on plants and animals, and establish non-binding criteria for concentrations of contaminants in effluent streams. This information can then be used to derive the regulatory requirements that may be incorporated into permit conditions, thereby becoming binding standards. In some cases limitations more stringent than the technology-based requirements can be imposed.

2.3.1 Human Health Standards-Water, Fish & Carcinogen

Standards set to prevent adverse health effects in humans and minimize exposure to carcinogens. Level below which no adverse health effect to humans is expected, based on tests assuming an ingestion rate of 2 liters of water and 6.5 grams of fish per day. The limit represents the human health criteria for carcinogens at the 1.0E-06 level, assuming a lifetime consumption of 6.5 g/day average of contaminated fish and/or shellfish for a 70-kg male person.

2.3.2 Chronic Freshwater Limits - Lowest Effect Level

Standards set to prevent acute or chronic effects on aquatic life. Concentration below which chronic or latent adverse effects will not appear in freshwater biota. The data is insufficient to derive criteria. The stated limit is the lowest observed effect level.

2.3.3 Chronic Freshwater Limits - 96 Hour Average

Standards set to prevent acute or chronic effects on aquatic life. Concentration below which chronic or latent adverse effects will not appear in freshwater biota. The limit is the maximum 96-hour average, not to be exceeded more than once every 3 years.

2.3.4 Human Health Standards - Water & Fish Ingestion

Standards set to prevent adverse health effects in humans and minimize exposure to carcinogens. Level below which no adverse health effect to humans are expected, based on tests assuming ingestion rate of 2 liters of water and 6.5 grams of fish per day.

2.3.5 Chronic Marine Limits - Lowest Effect Level

Standards set to prevent acute or chronic effects on aquatic life. Concentration below which chronic or latent adverse effects will not appear in freshwater biota. The data is insufficient to derive criteria. The stated limit is the lowest observed effect level.

2.3.6 Chronic Freshwater Limits

Standards set to prevent acute or chronic effects on aquatic life. Concentration below which chronic or latent adverse effects will not appear in freshwater biota.

2.4 SAFE DRINKING WATER ACT, 42 USC Section 300, et seq.

The Safe Drinking Water Act (SDWA) establishes maximum contaminant levels or MCL's and Secondary MCL's for discharges to public drinking water in 40 CFR 141 and 40 CFR 143. The SDWA is often incorporated into other regulations by reference. MCL's protect the health of persons by regulating the maximum level of the contaminant permitted in community drinking water. Secondary MCL's protect the public welfare by regulating the aesthetic qualities of water in community and noncommunity water systems. In addition, the SDWA (40 CFR 148) regulates the underground injection of hazardous wastes. These limits correspond to the land disposal restrictions contained in RCRA (40 CFR 268).

2.4.1 MCLs-Inorganics

40 CFR 141 establishes maximum contaminant levels or MCL's for public drinking water. This regulation protects the health

of persons by regulating the inorganic contaminants in drinking water in community and noncommunity drinking water systems. Turbidity in drinking water is also regulated by 40 CFR 141.

2.4.2 MCLs-Organics

40 CFR 141 establishes maximum contaminant levels or MCL's for public drinking water. This regulation protects the health of persons by regulating the organic contaminants in drinking water in community and non-transient noncommunity drinking water. Turbidity in drinking water is also regulated by 40 CFR 141.

2.4.3 SMCLs - Organics

40 CFR 143 establishes secondary maximum contaminant levels, SMCLs, which are unenforceable federal guidelines regarding taste, odor, color, and certain other non-aesthetic effects of drinking water.

2.5 CLEAN AIR ACT, 40 USC 7401 et seq.

The federal Clean Air Act (CAA), originally enacted in 1970, has been amended several times over the years. It is one of the most complex environmental statutes existing. The intent of the act is to protect and enhance the quality of the nation's air resources in order to promote the public health and welfare and the productive capacity of its population. To achieve this goal, the act requires that the EPA establish air quality standards, and states develop state implementation plans. Since the act was substantially amended in 1990, many of EPA's implementing regulations have yet to be promulgated. These standards control

air quality through various mechanisms including the National Ambient Air Quality Standards (NAAQS) and emission limitations.

Section 112 of the CAA and EPA's implementing regulations (40 CFR 61) provide control of the emission of hazardous pollutants to the atmosphere. This control is through the adoption of National Emission Standards for Hazardous Air Pollutants (NESHAP). Approval to construct a new facility or to modify an existing one may be required by these regulations. NESHAPs apply to existing as well as new sources. Pollutants regulated under NESHAPs may not be emitted from enough sources to justify a NAAQS and thus are controlled through this separate provision.

EPA's National Ambient Air Quality Standards manages air pollution through the use of controls based upon ambient air concentrations of pollutants in an area. (Section 109 of the CAA) The NAAQS establish the maximum allowable concentration for certain criteria pollutants and compel the degree of source control to meet the standard. The NAAQS are not directly enforceable; rather they set the standards on which other enforceable requirements, such as emission limitations and permit requirements, are based. The standards are classified as either primary or secondary.

Primary standards are set to protect human health with an "adequate margin of safety." Secondary standards are set to protect the "public welfare." Public welfare is defined extremely broad, including "effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather,

visibility, and climate..." (42 USC section 7602(h) and 40 CFR 50)). In general, if an area is currently attaining the NAAQS standards established, the Prevention of Significant Deterioration (PSD) permit program will apply. If an area is a "non-attainment" area, then a permit must be sought under the non-attainment permit program. New sources of emissions must comply with New Source Performance Standards (NSPS) (Section 111 of CAA and 40 CFR 60). The NSPSs are technology driven standards and may incorporate and require use of PSD permits.

2.6 DOE ORDER 5400.5 - RADIATION PROTECTION OF THE PUBLIC AND THE ENVIRONMENT

DOE Order 5400.5, Radiation Protection for the Public and the Environment, establishes standards and requirements for operations of the DOE and DOE contractors with respect to protection of members of the public and the environment against undue risk from radiation.

2.6.1 Air Inhalation DCG - 0.5 Days Retention

The Derived Concentration Guide (DCG) values for inhalation of air assume that under conditions of continuous exposure, members of the public will to inhale 8400 cubic meters of air. The DCG values are based on a committed effective dose equivalent of 100 mrem for the radionuclide taken into the body by inhalation during one year, and are assigned to lung retention class "D", which has a removal half-time of 50 days. [See International Council on Radiation Protection (ICRP) Publication 30 for the Task Group Lung Model.] If more than one limit is

given for a contaminant, the most restrictive or smaller is reported.

2.6.2 Air Inhalation DCG - 50 Days Retention

The DCG values for inhalation of air assume, under conditions of continuous exposure, members of the public are assumed to inhale 8400 cubic meters of air. The DCG values are based on a committed effective dose equivalent of 100 mrem for the radionuclide taken into the body by inhalation during one year, and are assigned to lung retention class "W", which has a removal half-time of 50 days. (See ICRP Publication 30 for the Task Group Lung Model.) If more than one limit is given for a contaminant, the most restrictive or smaller is reported.

2.6.3 Air Inhalation DCG - 500 Days Retention

The DCG values for inhalation of air assume, under conditions of continuous exposure, members of the public are assumed to inhale 8400 cubic meters of air. The DCG values are based on a committed effective dose equivalent of 100 mrem for the radionuclide taken into the body by inhalation during one year, and are assigned to lung retention class "Y", which has a removal half-time of 50 days. (See ICRP Publication 30 for the Task Group Lung Model.) If more than one limit is given for a contaminant, the most restrictive or smaller is reported.

2.6.4 Water Ingestion DCG

The DCG values for ingestion of water assume, under conditions of continuous exposure, members of the public are assumed to ingest 730 liters of drinking water. The DCG values are based on a committed effective dose equivalent of 100 mrem

for the radionuclide taken into the body by ingestion during one year, and are not release limits, but rather are screening values for considering best available technology (BAT) for discharges and for making dose estimates. For liquid wastes containing radionuclides from DOE activities which are discharged to surface water, the BAT is the prescribed level of treatment if the surface waters contain, at the point of discharge and prior to dilution, radioactive material at annual average concentrations greater than the DCG values given. Additional treatment is not required for waste streams that contain radioactive concentrations of not more than the DCG values at the point of discharge to a surface waterway. For liquid waste streams containing more than one type of radionuclide, the DCG shall be the sum of the fractional DCG values, and if more than one limit is given for a contaminant, the most restrictive or smaller is reported.

3.0 SPECIFIC COMPONENT REGULATIONS

Based on the regulations described above and using lists of components identified in biomass conversion process effluents [Elliott 1992, Fagernas 1992], the following two tables were prepared. These tables were derived from searches using the ReOpt™ software [White & Bryant 1992]. The tables list the components determined to be regulated based on any of the regulations described above. These tables can be used as a reference for determining required actions relative to process effluents which might contain any of the listed components.

Tables 1 and 2 provide a basis for evaluation of biomass thermochemical conversion process effluents. Some of the regulations do not specifically apply to these effluents, partly because the processes are not yet commercialized and have not been the target of regulators. In addition, there are no stream specific definitions of the biomass conversion effluents yet designated however, it is possible the such designation will be forthcoming based on the amounts and types of hazardous chemicals that have been identified in the biomass conversion effluents. The information in Tables 1 and 2 should be helpful in the future definition of applicable regulations for these effluents.

ReOpt™ Version 2.0, Pacific Northwest Laboratory, Richland, WA

TABLE 1. APPLICABLE FEDERAL REGULATIONS

ORGANIC CONTAMINANTS

Contaminant	CAS No.	Statute	Regulation	Limit
Acetaldehyde (ethanal)	75-07-0	RCRA	LDR/physical characteristic	specified technol. 1000 mg/kg
Ethyl Acetate	141-78-6	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U112	specified technol. NA
Lead Acetate	301-04-2	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U144	specified technol. NA
Acetone	67-64-1	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U002	specified technol. NA
Acetophenone	98-86-2	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U004	specified technol. NA
Acrylic Acid (2-propenoic acid)	79-10-7	RCRA	LDR/physical characteristic	specified technol. 1000 mg/kg
Ethylacrylate	180-88-5	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U113	specified technol. NA
Ethylmethacrylate	97-63-2	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U118	specified technol. NA
Methylmethacrylate	80-62-6	RCRA	LDR/physical characteristic	specified technol. 1000 mg/kg
Aniline	62-53-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U012	specified technol. NA
Benzene	71-43-2	RCRA	Toxicity characteristic/HW No. D018 LDR/physical characteristic Hazardous Chemical/HW No. U019	0.5 mg/L specified technol. NA
		CWA	Human health standards-water, fish, & carcinogen	0.66µg/L
		SDWA	MCL - Organics	0.005 mg/L
Methylbenzene (Toluene)	108-88-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U220	specified technol. NA
		CWA	Chronic marine limits-lowest effect level	5000µg/L
		SDWA	MCL-Organic	1.0 mg/L
Dimethylbenzene (xylene)	1330-20-7	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U239	specified technol. NA
		SDWA	MCL-Organic *(xylenes total)*	10 mg/L

TABLE 1. APPLICABLE FEDERAL REGULATIONS, cont.

ORGANIC CONTAMINANTS

Contaminant	CAS No.	Statute	Regulation	Limit
1-Methylethylbenzene (isopropylbenzene, cumene)	98-82-8	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U055	specified technol. NA
1,2-Dihydro-3-methylbenz(j) aceanthrylene (3-methylcholanthrene)	56-49-5	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U157	specified technol. NA
Benz(a)anthracene	56-55-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U018	specified technol. NA
7,12-Dimethylbenz(a) anthracene	57-97-6	RCRA	LDR/physical characteristic	specified technol. 1000 mg/kg
Benzo(a)pyrene	50-32-8	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U022	specified technol. NA
1-Butanol	71-36-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U031	specified technol. NA
2-Butenal	4170-30-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U053	specified technol. NA
Chrysene	218-01-9	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U050	specified technol. NA
Creosote	8001-58-9	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U051	specified technol. NA
Cresol (cresylic acid)	1319-77-3	RCRA	Toxicity characteristic/HW No. D026 LDR/physical characteristic Hazardous Chemical/HW No. U052	200 mg/L specified technol. NA
ortho-Cresol	95-48-7	RCRA	Toxicity characteristic/HW No. D023 LDR/physical characteristic	200.0 mg/L specified technol.
meta-Cresol	108-39-4		Toxicity characteristic/HW No. D024 LDR/physical characteristic	200.0 mg/L specified technol.
Cyclohexane	110-82-7	RCRA	Toxicity characteristic/HW No. D026 LDR/physical characteristic Hazardous Chemical/HW No. U056	200 mg/L specified technol. NA
Cyclohexanone	108-94-1	RCRA	LDR/physical characteristic Hazardous Chemical/HW. No. U057	specified technol. NA

TABLE 1. APPLICABLE FEDERAL REGULATIONS, cont.

ORGANIC CONTAMINANTS

Contaminant	CAS No.	Statute	Regulation	Limit
Dibenz(a,h)anthracene	53-70-3	RCRA	LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U063	NA
Dibenz(a,i)pyrene	189-55-9	RCRA	LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U064	NA
2,4-Dimethylphenol	105-67-9	RCRA	LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U101	NA
Fluoranthene	206-44-0	RCRA	LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U120	NA
		CWA	Chronic marine limits-lowest effect level	16μg/L
Formaldehyde	50-00-0	RCRA	LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U122	NA
Formic acid	64-18-6	RCRA	LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U123	NA
Furan	110-00-9	RCRA	LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U124	NA
Tetrahydrofuran	109-99-9	RCRA	LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U213	NA
Furfural	98-01-1	RCRA	LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U125	NA
Indenal(1,2,3-cd)pyrene	193-39-5	RCRA	LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U137	NA
2-methyl-propanol	78-83-1	RCRA	LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U140	NA
Methanol	67-56-1	RCRA	LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U154	NA
Methylethylketone	78-93-3	RCRA	Toxicity characteristic/HW No. D035	200 mg/L
			LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U159	NA
4-Methyl-2-pentanone (methylisobutylketone, MIBK)	108-10-1	RCRA	LDR/physical characteristic	specified technol.
			Hazardous Chemical/HW No. U161	NA

TABLE 1. APPLICABLE FEDERAL REGULATIONS, cont.

ORGANIC CONTAMINANTS

Contaminant	CAS No.	Statute	Regulation	Limit
Naphthalene	91-20-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U165	specified technol. NA
		CWA	Chronic freshwater limits-lowest effect level	620μg/L
1,4-Naphthalenedione (naphthoquinone)	130-15-4	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U166	specified technol. NA
Phenol	108-95-2	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U188	specified technol. NA
1,3-Benzenediol (resorcinol)	108-46-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U201	specified technol. NA
2-Propenol (allyl alcohol)	107-18-6	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. P005	specified technol. NA
2-Propenal (acrolein)	107-02-8	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. P003	specified technol. NA
		CWA	Chronic freshwater limits-lowest effect level	21μg/L
Quinone (2,5-cyclohexadiene-1,4-dione)	106-51-4	RCRA	LDR/physical characteristic Hazardous Chemical/HW.No. U197	specified technol. NA
Pyridine	110-86-1	RCRA	Toxicity characteristic/HW No. D038 LDR/physical characteristic Hazardous Chemical/HW No. U196	5.0 mg/L specified technol. NA
Methylpyridine	109-06-8	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U191	specified technol. NA
Aziridine (ethylenimine)	151-56-4	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. P054	specified technol. NA
2-Methylaziridine	75-55-8	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. P067	specified technol. NA
Nicotine	54-11-5	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. P075	specified technol. NA

TABLE 2. APPLICABLE FEDERAL REGULATIONS

INORGANIC COMPONENTS

Contaminant	CAS No.	Statute	Regulation	Limit
Arsenic	7440-38-2	RCRA	Toxicity characteristic/HW No. D004	5.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D004	5.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/CA list-metals	500 mg/L
			LDR/toxicity characteristic-nonwastewater extract/HW No. D004	5.0 mg/L
		CWA	Human health standards-water, fish, & carcinogen	0.0022μg/L
		SDWA	MCL - inorganic	0.05 mg/L
		DOE Order 5400.5	Air Inhalation DCG-50 days retention	0.5μCi/mL
Barium	7440-39-3	RCRA	Toxicity characteristic/HW No. D005	100.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D005	100.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/toxicity characteristic-nonwastewater extract/HW No. D005	100.0 mg/L
		CWA	Human health standards-water & fish ingestion	1000μg/L
		SDWA	MCL - inorganic	2.0 mg/L (a)
		DOE Order 5400.5	Air Inhalation DCG-0.5 days retention	0.1μCi/mL
Cadmium	7440-43-9	RCRA	Toxicity characteristic/HW No. D006	1.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D006	1.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/CA list-metals	100 mg/L
			LDR/toxicity characteristic-nonwastewater extract/HW No. D006	1.0 mg/L
			LDR/toxicity characteristic-specified technology	specified technol.
		CWA	Chronic freshwater limits-96 hour average	1.1μg/L
		SDWA	MCL - inorganic	0.005 mg/L
		DOE Order 5400.5	Air Inhalation DCG-0.5 days retention	0.05μCi/mL
			Air Inhalation DCG-50 days retention	0.05μCi/mL
			Air Inhalation DCG-500 days retention	0.05μCi/mL
Chromium	7440-47-3	RCRA	Toxicity characteristic/HW No. D007	5.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D007	5.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/CA list-metals	500 mg/L
			LDR/toxicity characteristic-nonwastewater extract/HW No. D007	5.0 mg/L
		SDWA	MCL - inorganic	0.1 mg/L
		DOE Order 5400.5	Water Ingestion DCG	0.01μCi/mL
			Air Inhalation DCG-0.5 days retention	0.1μCi/mL
			Air Inhalation DCG-50 days retention	0.1μCi/mL
			Air Inhalation DCG-500 days retention	0.1μCi/mL

TABLE 2. APPLICABLE FEDERAL REGULATIONS, cont.

INORGANIC COMPONENTS

Contaminant	CAS No.	Statute	Regulation	Limit
Lead	7439-92-1	RCRA	Toxicity characteristic/HW No. D008	5.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D008	5.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/CA list-metals	500 mg/L
			LDR/toxicity characteristic-nonwastewater extract/HW No. D008	5.0 mg/L
			LDR/toxicity characteristic-specified technology	specified technol.
		CAA	NAAQS primary standards - calendar quarter	micro-gm/m3
			NAAQS secondary standards - calendar quarter	1.5μg/m3
		CWA	Chronic freshwater limits-96 hour average	3.2μg/L
		SDWA	MCL - inorganic	TT (b) (c)
		DOE Order 5400.5	Air Inhalation DCG-0.5 days retention	0.2μCi/mL
Mercury	7439-97-6	RCRA	Toxicity characteristic/HW No. D009	0.2 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D009	0.2 mg/L
			LDR/physical characteristic	specified technol.
			LDR/CA list-metals	20 mg/L
			LDR/toxicity characteristic-nonwastewater extract/HW No. D009	0.20 mg/L
			LDR/toxicity characteristic-specified technology	specified technol.
		CWA	Chronic freshwater limits-96 hour average	0.012μg/L
		SDWA	MCL - inorganic	0.002 mg/L
		DOE Order 5400.5	Air Inhalation DCG-0.5 days retention	0.02μCi/mL
			Air Inhalation DCG-50 days retention	0.02μCi/mL
Selenium	7782-49-2	RCRA	Toxicity characteristic/HW No. D010	1.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D010	1.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/wastewater-mixtures/HW No. F039	0.82 mg/L
			LDR/CA list-metals	100 mg/L
			LDR/toxicity characteristic-nonwastewater extract/HW No. D010	5.7 mg/L
		CWA	Human health standards - water & fish ingestion	10μg/L
		SDWA	MCL - inorganic	0.05 mg/L
		DOE Order 5400.5	Water ingestion DCG	0.05μCi/mL
			Air Inhalation DCG-0.5 days retention	0.8μCi/mL
			Air Inhalation DCG-50 days retention	0.8μCi/mL

TABLE 2. APPLICABLE FEDERAL REGULATIONS, cont.

INORGANIC COMPONENTS

Contaminant	CAS No.	Statute	Regulation	Limit
Silver	7440-22-4	RCRA	Toxicity characteristic/HW No. D011	5.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D011	5.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/toxicity characteristic-nonwastewater extract/HW No. D011	5.0 mg/L
		CWA	Chronic freshwater limits	0.12μg/L
		SDWA	SMCL - inorganic	0.1 mg/L
		DOE Order 5400.5	Air Inhalation DCG-0.5 days retention	0.05μCi/mL
			Air Inhalation DCG-50 days retention	0.05μCi/mL
			Air Inhalation DCG-500 days retention	0.05μCi/mL

(a) Effective Date:January 1 ,1993
(b) Effective Date/December 7, 1992
(c) TT=Treatment technique requirement in effect.

4.0 FUTURE UPDATING OF THE REGULATORY ENVIRONMENT

Evaluation of the regulatory environment surrounding biomass thermochemical conversion processes is an ongoing activity in this project. This report is the revised version of the original report issued in January 1993, updated in August 1993 with the updates for June 1993 through February 1994 included here. This report will be updated on a semi-annual basis to include changes in the regulations that might affect a biomass thermochemical conversion facility. Significant changes in some of the regulatory requirements have been proposed and may become effective within the next year. The following highlights a portion of the anticipated regulatory changes.

4.1 Resource Conservation and Recovery Act Update:

- The EPA proposes to revise the existing small-scale treatability studies Subtitle C exclusions to allow up to 10,000kg of soil and debris contaminated with non-acute hazardous waste from a single waste stream to be treated. (40 CFR 261)

- The EPA plans to establish air emission standards for emissions of volatile organics from tanks and impoundments at hazardous waste TSD facilities and require that organic emissions controls be installed and operated. (40 CFR 264/265)

- The EPA plans to amend Subpart F groundwater monitoring regulations to foster the early detection of leaks and to

better tailor the current groundwater monitoring regulations to site-specific conditions. (40 CFR 264/265)

- The EPA proposes treatment standards under the RCRA land disposal restrictions (LDR) program for certain newly listed wastes and contaminated debris pursuant to a proposed consent decree and finalizes revised treatment standards for other hazardous debris. (40 CFR 268)

- EPA proposes procedures and technical requirements for implementing corrective action at RCRA solid waste management units. The proposal would create a new Subpart S to define requirements for conducting remedial investigations, evaluating potential remedies, and selecting and implementing remedies at RCRA facilities.

4.2 Clean Water Act Update:

- EPA proposes two options for determining which facilities newly identified under CWA section 304(l) are required to have individual control strategies: 1) require ICSs only for point sources originally subject to such a requirement or 2) give the state discretion to determine eligibility on a case by case basis. (40 CFR 130)

4.3 Safe Drinking Water Act Update:

- Primary Drinking Waster Regulations - Radionuclides: The EPA has proposed MCLGs of zero and the MCLs for several

radionuclides as well as additional monitoring, reporting, and public notification requirements. (Final rule 10/94)

- EPA set MCLs and MCLGs for 18 synthetic organic chemicals and five inorganic chemicals. The NPDWRs consist of MCLs and monitoring, reporting and public notification requirements. [40 CFR 141/142/143, effective 1/17/94]

4.4 Clean Air Act Update:

- The EPA proposes to revise the maximum allowable increases for particulate matter under the requirements for prevention of significant deterioration. (40 CFR 51/21)

- EPA proposes general provisions for NESHAPs under Sect. 112 which codify procedures and criteria to implement emission standards for stationary sources that emit one or more of the 189 substances listed as hazardous air pollutants. The general provisions eliminate the need to repeat general information and requirements within the standards. (40 CFR 60, 61, and 63)

- The EPA has proposed to control emissions of hazardous organic chemicals from storage tanks, process vents, equipment leaks, transfer operations, and wastewater treatment of synthetic organic chemicals manufacturing plants. (40 CFR 63)

- List of substances and threshold quantities for accidental release prevention: EPA proposed a list of regulated

substances as required under Sect. 112(r) of the CAA. Included are 100 toxic substances, 62 flammable substances, and commercial explosives. Threshold quantities for accidental releases for each substance listed were also proposed. (40 CFR 68)

5.0 REFERENCES

Elliott, D. C. Evaluation of Wastewater Treatment Requirements for Thermochemical Biomass Liquefaction. NREL/TP-421-4715, National Renewable Energy Laboratory: Golden, Colorado, April 1992.

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White, M. K. and J. L. Bryant. ReOpt™ V2.0 User Guide. Pacific Northwest Laboratory: Richland, Washington, October 1992.

Statutes:

Clean Air Act (CAA), 40 USC 7401, et seq.

Clean Water Act (CWA), 33 USC 1251, et seq.

National Environmental Policy Act (NEPA), 42 USC 4321, et seq.

Resource Conservation and Recovery Act of 1976 (RCRA), 42 USC 6901, et seq.

Safe Drinking Water Act (SDWA), 42 U.S.C. 300, et seq.

Regulations:

40 CFR 60. 1992. "Standards of Performance for New Stationary Sources," U.S. Code of Federal Regulations.

40 CFR 61 "National Emission Standards for Hazardous Pollutants." U.S. Code of Federal Regulations.

40 CFR 104-149 "Subchapter D - Water Programs," U.S. Code of Federal Regulations.

40 CFR 141 "National Primary Drinking Water Standards," U.S. Code of Federal Regulations.

40 CFR 257 "Criteria for Classification of Solid Waste Disposal Facilities and Practices.

40 CFR 261 "Identification and Listing of Hazardous Waste," U.S. Code of Federal Regulations.

40 CFR 262 "Standards Applicable to Generators of Hazardous Waste," U.S. Code of Federal Regulations.

40 CFR 264 "Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities," U.S. Code of Federal Regulations.

40 CFR 266 "Standards for the Management of Specific Hazardous Wastes and Specific Types of Hazardous Waste Management Facilities," U.S. Code of Federal Regulations.

40 CFR 268 "Land Disposal Restrictions," U.S. Code of Federal Regulations.

40 CFR 270 "EPA Administered Permit Programs: The Hazardous Waste Permit Program," U.S. Code of Federal Regulations.

49 CFR 171-180 "Hazardous Materials Regulations," U.S. Code of Federal Regulations

57 FR 60920-60921, December 22, 1992. "Water Quality Standards," Federal Register.

Results of Toxicological Testing of Whole Wood Oils Derived from the Fast Pyrolysis of Biomass

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Disclamer: This is a pre-paper that is in preparation at NREL to summarize the state of knowledge on the environmental and health impacts of pyrolysis oils. It is being circulated at the Specialists meeting Biomass Pyrolysis Oil Properties and Combustion being held in Estes Park, September 26-28, 1994 so that the technical development community in the field can provide their comments and criticism prior to release. Please pass all comments to David Gratson at NREL. NOTE: This paper contains new information and analysis which has not yet been reviewed-it is given to you on the understanding that you will not CITE it or REPRODUCE it without the permission of the Author.

Abstract

The National Renewable Energy Laboratory initiated toxicological testing for two whole wood oil samples (Southern Pine and Oak) produced in the vortex pyrolysis reactor at our facilities. This first phase of testing was performed to develop a toxicological profile, following a protocol appropriate for industrial compounds/products not intended to be used as consumer producsts. The tests conducted included dermal toxicity, eye irritation, inhalation toxicity and Ames mutagenicity and was done with the consultation of Mr. John Butala, Duquesne University. Results of this toxicological testing will be presented and compared with available data obtained from testing of similar material by other researchers. The results of NREL's testing showed that these materials may be handled safely with commonly used safe work practices and personal protective devices.

Introduction and Background

The development of any new product and process entails consideration of environmental impacts. Biocrude (the raw oil derived from pyrolysis of biomass) offers the possibility of a renewable fuel for both transportation and power production. However, it must be developed in a manner that minimizes environmental impacts both on human health and the environment. This paper discusses the toxicological properties of biomass-derived oils, and in particular, whole-wood oils produced at the National Renewable Energy Laboratory (NREL) vortex pyrolysis unit. Information on toxicological properties is essential for the establishment of worker and consumer protection as well as for regulatory compliance.

Biomass pyrolysis oils are an extremely complex mixture of compounds, each of which individually and collectively affect the toxicological properties of the whole oil. Process conditions (especially temperature and residence time) as well as feedstocks greatly influence the resulting products. However, pyrolysis oils generally have been characterized into several fractions, each of which is usually dominated by certain compounds which contain characteristic functional groups. Several researchers have attempted to separate and characterize these oils for commercial as well as toxicological information. Piskorz and Scott (1) classified fast pyrolysis oils from their fluidized-bed reactor, operated from 450-550° C and residence time of 0.5 seconds. They were able to characterize

80-90 wt. % of the oils and categorized them into four major groups; sugars and anhydrosugars, carbonyl and hydroxycarbonyl compounds, acids including formic and acetic, and "pyrolytic" lignin compounds. Similar compounds have been shown by Evans and Milne (2) who identified products from these primary pyrolitic oils as well as from oils obtained at more aggressive temperatures. Using a benchscale reactor with analysis by molecular beam mass spectrometry they identified pyrolysis products from pine wood at three temperatures (see figures 1-3). Residence times for all three were approximately 750 milliseconds. The primary pyrolysis oils produced from pine wood at 500° C included those noted by Piskorz and Scott. However, at 700° C major changes were observed. Low molecular weight alkenes are formed as well as some aromatics including furan, benzene, toluene, phenol, and phenolic secondary products from lignin cracking. At 950° C, formation of benzene and heavyer aromatics is observed. These include naphthalene, anthracene through fluoranthene and up to perylene. These highly condensed aromatics are typical of that observed in gasifier tars. Fig. 1 show mass spectrometric fingerprints for the fast pyrolysis vapors under the range of conditions discussed. These are not quantitative but give a feeling for the range of compounds involved.

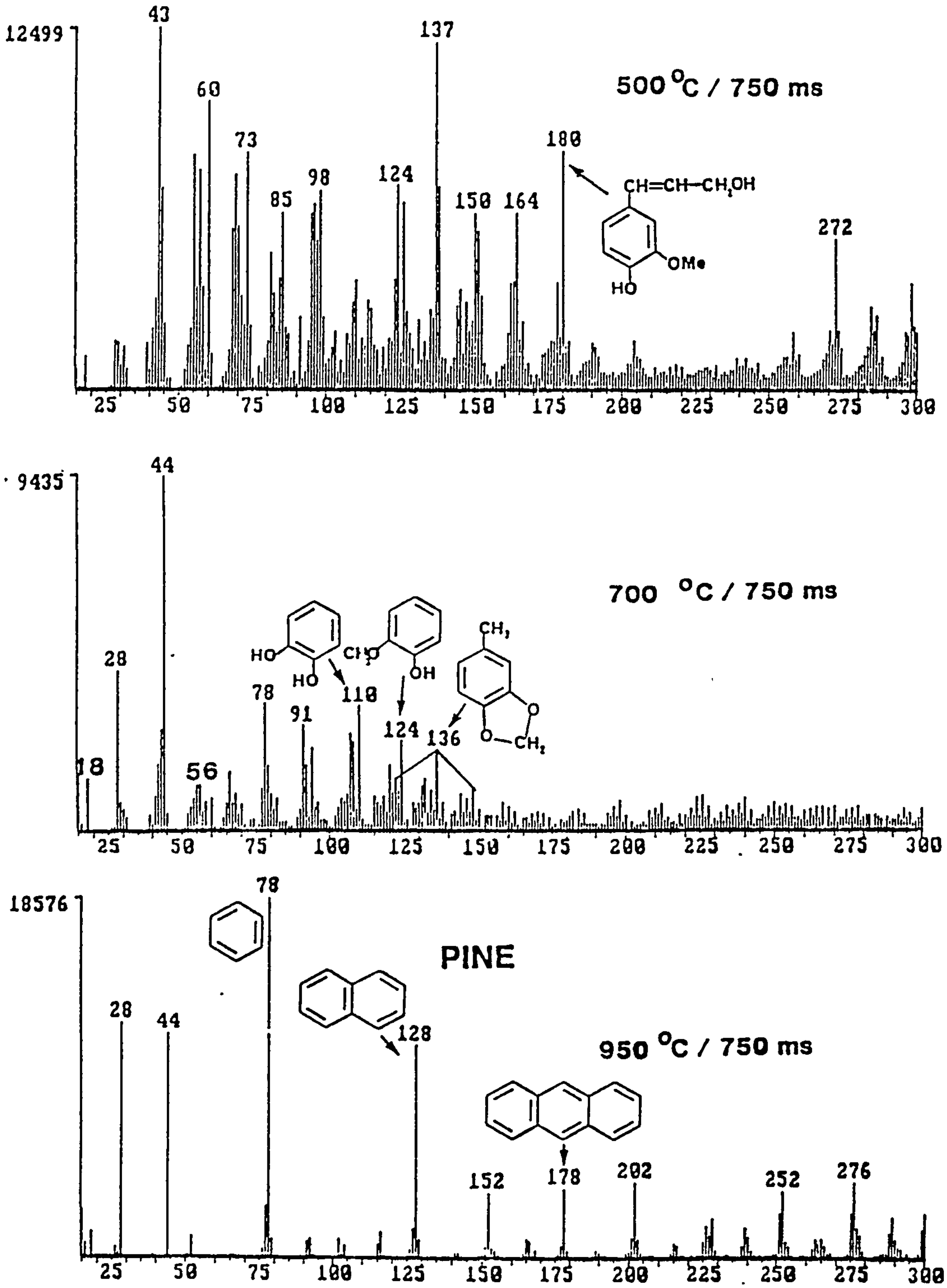
Several groups, (3-6), have worked to characterize the toxicology of biomass-derived gases, oils and tars. Processing conditions for these products have involved kilns, gasification, and pyrolysis. Duncan collected samples from three gasifiers, one updraft fixed bed, and two updraft fluidized beds for toxicological study. Unable to satisfactorily separate the fractions for individual study, his team instead tested whole tar samples. Duncan's interpretation was that all samples showed mutagenic activity without metabolic activation, for plate loadings of 50-2500 μg/plate, using the Ames mutagenicity test. This test is a widely used, quick, and relatively inexpensive assay of the potential of the test material to induce genetic damage in the cell. Duncan's data indicated that the most highly mutagenic samples correlated with the higher process conditions (900° C), and that weaker positive results were obtained with samples operating in the 750-800° C range.

Elliott subsequently reviewed Duncan's data as part of his study, which included both pyrolysis and gasification samples. Elliott concluded that no mutagenic activity was evident in Duncan's data at the low concentration range (50-500 μg/plate). At the higher concentration ranges, acute toxicity in the cultures was evident rendering any interpretation impossible. Elliott used samples from entrained-flow pyrolysis, updraft gasification, downdraft gasification, and fluidized-bed gasification. (See Table 1 for systems and conditions).

Elliott's toxicological data from these samples included both Ames mutagenicity and skin tumor studies. The results of the Ames study showed no activity for any of the aqueous samples, even those from the fluidized-bed gasifier which contained polyaromatic hydrocarbons (PAH's). This was true even though the aqueous samples were studied at high concentrations to compensate for the dilute state of these samples. For the condensate samples, only the Battelle Columbus Laboratories (BCL) tars (both pine and hardwood) exhibited activity above the controls. Concentrations for these tests were from 2-500 μg/plate, with the NREL tests performed at up to 2500 μg/plate. However, killing of the cultures occurred at concentrations above 1000 μg/plate .

Elliott studied several of the condensate samples for evidence of skin tumor initiation. BCL hardwood and pine tars caused tumors in all animals, with tumors appearing earlier and in greater quantity than those seen on the benzo(a)pyrene (BaP) positive control group. Back calculation from the analysis of the BCL tars showed that the animals received approximately four times the amount of BaP as those in the positive control group. The NREL cracked tar showed lower tumor activity,

Figure 1. Mass Spectra, by Molecular Beam Mass Spectrometry, From Pine Wood at the Temperatures Listed



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which may have been the result of the lower number of four-ring and larger PAH compounds. The Rome, Georgia, and Cal Recover, and the NREL primary oils did not exhibit tumors above the background control group. The Rome, Georgia, tar contained substantial quantities of oxygenated aromatics, which Elliott believed may have had the possibility for tumor promotion. No activity was seen in the limited number of aqueous samples tested.

In general, Elliott only found biological toxicity with the high-temperature processed tars. His Ames testing only showed positive activity for tars generated above 800° C. The skin tumor initiation test revealed limited activity for tars down to 750° C. This activity correlated with higher molecular weight (four-ring and above) PAH's.

Laboratory Testing of NREL Vortex Reactor Primary Oil

In 1993, NREL sponsored toxicological testing of biomass-derived products for its biomass power program, in order to develop a toxicological profile. These tests were performed on two different whole-wood oils (WWOs) designated WWO#1 and WWO#2, which were obtained under the conditions shown in Table 2. No fractionation was performed This testing supported an initial health hazard assessment for acute overexposure, while also permitting the generation of preliminary warning labels. The acute hazards are those resulting from laboratory accidents such as spills and splashes. John Butala, a toxicologist affiliated with Duquesne University, provided guidance for the tests; most of the results noted below have been taken directly from his report to NREL. Sitek Research Laboratories of Rockville, Maryland, performed the Ames assay. International Research and Development Corporation of Mattawan, Michigan, performed the mammalian tests. The individual tests consisted of eye irritation, dermal and inhalation acute toxicity, and Ames mutagenicity. The eye irritation test demonstrates the ability of the test material to cause irritation and damage following direct contact. Also, it evaluates the effectiveness of first-aid techniques such as eye washing. The dermal and the inhalation acute toxicity test evaluates the potential of a material to cause systematic toxicity or death with skin contact and/or vapor inhalation. The object of the dermal test is to discover whether or not the test substance can move effectively through the skin; the effect of the material on the skin itself is not evaluated other than for signs of obvious damage. The Ames testing is a preliminary assessment of the potential of the test material to induce genetic toxicity.

The oils submitted for this testing were produced by the NREL fast-pyrolysis process. The NRELprocess uses high velocity carrier gas to entrain biomass particles into a vortex reactor. The particles are centrifuged against the reactor wall, typically held at about 600° C. Heating occurs by solid convective heat transfer resulting in a rapid ablative pryrolysis. The biomass particle depolymerizes to a liquid that quickly vaporizes from the reactor surface. The oil vapors leave the reactor within about 30 milliseconds at a temperature of 500° C, and then enter a vapor cracker tube. When desired the vapor cracker can subject the oils to additional cracking to further modify the chemistry. However, at the operating temperatures for these runs, the object was just to prevent the vapors from condensing before the collection points. After passing through the vapor cracker the product enters a series of heat exchangers where the oils are condensed.

Table 1. Reactor Systems in Elliott's Study

Sample	*GA Tech Oil*	*NREL primary Oil*	*NREL cracked Oil/Tar*	*Rome, GA Tar*	*Univ. Fl Tar*	*Rocky Creek Tar*	*Cal Recovery Tar*	*Univ. MO Tar*	*PNL Fluid Bed Tar*	*IGT* Fluid Bed Tar*	*BCL Tar*	*BCL Tar*
Reactor	entrained flow pyrolysis	entrained flow pyrolysis	vapor-phase cracker entrained flow pyrolysis	updraft, air blown gasifier	down-draft, air blown gasifier	down draft, air blown gasifier	down-draft, air blown gasifier	fluid-bed, steam blown gasifier	dual-fluid/bed gasifier	fluid-bed O_2-blown gasifier	entraine d flow gasifier	entraine d flow gasifier
Feedstock	ground oak	softwood sawdust	softwood pyr. vapors	hardwood chips	citrus chips	hardwood chips	walnut shells	oak sawdust	pine flake	maple	maple oak	pine
Reactor Temp. °C	424-477°	485°	750°	1650-1693 (°F?)	?	900°	540-573°	743°	750-780°	816°	900°	880°
Res. Time (sec)	4	?	0.3	?	?	?	?	~10	?	10	1.2	1.3
Sample Type	oil	oil	oil/tar	oil aqueous	overhead conden.	overhead conden.	cond., aqueous	scrub. water	cond., aqueous	cond., aqueous	tar	tar
Ames Results	⊖	⊖	⊖	⊖	⊖	⊖	⊖	⊖	⊖	⊖	⊕	⊕
Skin Tumor Results	not tested	very slight	⊕	⊕	not tested	not tested	⊖	not tested	not tested	not tested	⊕	⊕

*Institute of Gas Technology, Data adapted from Elliott.

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Table 2. **Reactor Conditions and Feedstocks used to generate NREL Samples**

Sample / Run	Feedstock	Pyrolysis Temperature	Vapor Cracker Temperature	Total Residence Time (seconds)
WWO#1, run 150	southern pine	625°C	510°C	0.8
WWO#2, run 154	oak	625°C	460°C	0.8

Results

The results from the toxicological testing indicated that both whole wood oils have a marked potential to induce serious and possibly irreversible eye damage following direct liquid contact, or contact with airborne droplets. In contrast, these materials showed no tendency to penetrate intact skin to cause internal organ damage or systemic toxicity following gross over-exposure. Acute airborne exposure and inhalation of high concentrations of these whole-wood oils can cause eye and lung damage; other signs of inhalation toxicity were reversible. Both materials showed mutagenic abilities in the Ames bacterial mutation assay. The tests also indicated that both WWO#1 and #2 have the potential to interact with cellular genetic material. Whether or not these substances have the ability to reach genetic targets within the cell nucleus of intact animals at effective (mutagenic) concentrations is unknown.

WWO#1 acted very aggressively on ocular tissue following direct application of 0.1 ml oil, undiluted. This oil damaged all parts of the eye structure in contact with it immediately following introduction. Washing with tap water for 30-40 seconds both diminished and delayed the maximal effect, but damage to the cornea occurred in all animals persisting to day 7 post-dosing, and to day 21 post-dosing in eight of nine animals. This oil then should be considered extremely irritating or corrosive to the eye. Because of the compositional and chemical similarities of WWO#2 with WWO#1 (notably pH), eye irritation testing on WWO#2 was cancelled. This oil will be assumed to be extremely irritating to the eye.

Both WWO#1 and WWO#2 at the maximum dose used in dermal toxicity testing failed to penetrate the intact skin and cause any signs of systemic toxicity. When applied to the skin for 24 hours at a dose of 2000 mg/kg (approximately 15% of body surface area), all animals survived to the end of the study. No adverse effects from the dermal treatment were noted. It should be noted that this testing is only concerned with movement of the material through the skin.

Whole-body inhalation exposure of animals to 3.3, 2.3, or 1.2 mg/L WWO#1 vapors and particulates in dynamic inhalation chambers for 4 hours produced sign of toxicity in all exposure groups. Two of 10 animals from the high-dose group and 1 of 10 from the mid-dose group died during the exposure or on day 1 following exposure. Lung changes (e.g.,discoloration and congestion) were noted in the animals that failed to survive. Corneal changes were noted in 7 of 10

high-dose animals and 4 of 10 mid-dose animals. The 4-hour inhalation LC_{50} (the lethal concentration for 50% of the animals) for WWO#1 is 3.1 mg/L, with 95% confidence limits of 2.4 and 4.2 mg/L. WWO#1 would be considered slightly toxic by acute inhalation. Because of the higher viscosity of WWO#2, the maximum concentration of airborne particles, within acceptable size range, was 1.4 mg/L. Lung and corneal changes identical to that with WWO#1 were noted. An LC_{50} value for this test material could not be established however, because more than 50% of the test animal population survived. WWO#2 would be considered at least moderately toxic by acute inhalation.

Mutagenic testing of WWO#1 in the Ames *Salmonella typhimurium* test indicated that this material was active (a greater than two fold increase over mean solvent control) as a mutagen both in the presence and absence of exogenous metabolic activation. Exogenous metabolic activation is the name given to a mixture of rat liver enzymes and coenzymes added to the test system to compensate for the lack of mammalian metabolic capacity in the bacterial test cells. Test material toxicity to the tester bacterial cells was demonstrated, so problems with solubility and bioavailability in test culture media are not a concern. Of the five bacterial tester strains, WWO#1 induced a clear-cut and moderately strong mutation response in one strain (TA-100) without metabolic activation at concentrations of 100 μg/plate and higher. With activation, WWO#1 induced a more pronounced mutagenic response in strain TA-100 (at 200 μg/plate) and also a moderate response in strains TA-98 (at 600 μg/plate) and TA-1538 (at 400 μg/plate). Range finding studies (tests which determine at which concentrations the mixtures induce acute toxicity to the bacterial cells) indicated that WWO#1 induced toxicity at concentrations of 550 ug/plate without activation and 1000 ug/plate with S-9. At this point in the data analysis, there is no particular significance to which bacterial tester strain responded positively in the test, or whether or not metabolic activation was required for the response. Identical testing with WWO#2 showed a clear-cut and moderately strong mutation response in strains TA-100 (at 50 ug/plate) and TA-1535 (at 500 μg/plate) without metabolic activation. With activation, WWO#2 induced a pronounced mutagenic response in strain TA-100 (at 500 ug/plate) and also moderate responses in strains TA-98 (at 100 μg/plate) and TA-1535 (at 500 μg/plate and higher). Range finding studies indicated that WWO#2 inducted toxicity at concentrations of 550 ug/plate without S-9 activation and 5000 μg/plate with activation. WWO#2 was slightly more potent in the Ames test than WWO#1. Each yielded about 1 revertant/μg in the presence of activation and about 0.5 or 0.2 revertants/μg in the absence of activation. By comparison, one of the positive control compounds, benzo(a)pyrene produced 600 and 1200 revertants/ug in the absence and presence of activation, respectively.

Table 3. **Regulatory Concerns with NREL Samples**

Regulatory Agency/Code	Warning Label: WWO#1	Warning Label: WWO#2
Occupational Safety and Health Administration	a HAZARDOUS substance (eye) not a HAZARDOUS substance, dermal a HAZARDOUS substance (inhalation	assume a HAZARDOUS substance (eye) not a HAZARDOUS substance (dermal) a HAZARDOUS substance (inhalation)
Department of Transportation	not a POISON B compound (dermal) not a POISON B by inhalation	not a POISON B compound (dermal) not a POISON B by inhalation
Consumer Product Safety Commission	SEVERE EYE IRRITANT and Corrosive Not TOXIC dermal TOXIC (inhalation)	assume SEVERE EYE IRRITANT and Corrosive Not TOXIC (dermal) TOXIC (inhalation)
Federal Insecticide Fungicide and Rodentia Act	TOXICITY CATEGORY I for eye irritation TOXICITY CATEGORY III for dermal toxicity TOXICITY CATEGORY III for inhalation	Assume TOXICITY CATEGORY I for eye irritation TOXICITY CATEGORY III for dermal toxicity TOXICITY CATEGORY III for inhalation

Evaluation of the above test results, which meet or exceed criteria for testing described by Consumer Product Safety Commission, Occupational Safety and Health Administration, U.S. Environmental Protection Agency in Federal Insecticide Fungicide and Rodentia Act, and U.S. Environmental Protection Agency Toxic Substance Control Act, Pesticide Assessment Guidelines Subdivision F Hazard Assessment Evaluation - Humans and Domestic Animals, and the OECD Guidelines for Testing Chemicals (1981), result in the issuance of warning labels for these materials. (see Table 3).

Discussion

The NREL sponsored testing described here has indicated the acute concern to workers (most notably, to their eyes-) in potential contact with biomass derived pyrolysis oils. This effect is probably a sole function of the pH of these oil, analysis of which has revealed a large concentration of acetic acid in the water-soluble fraction, as well as phenolic derivatives (as noted by Piskorz and Scott and others). This acute toxicity is certainly a matter of concern. Results of dermal toxicity testing however, are encouraging; these oils apparently have little potential for crossing the skin barrier. The LD_{50} (lethal dose at which 50% of the animals died) of greater than 2000 mg/kg for dermal toxicity is in contrast to phenol (850 mg/kg) and *p*-cresol (301 mg/kg). The inhalation testing showed similar results with the LC_{50} for WWO#1 of 3.1 mg/L, an order of magnitude greater than phenol (0.3 mg/L). One of the particularly interesting differences noted was the mutagenicity seen in the recent NREL samples; none however was observed by Elliott in the older NREL

samples. This is particularly puzzling, considering that the NREL cracked samples were produced at higher severity conditions (vapor cracker 750° C) than those in the recent NREL test. As Elliott has noted, mutagenic activity in gasification and pyrolysis condensates correlates with processing conditions (most notably production of PAHs). His data, obtained by gas chromatograph mass/ spectrometry (GC/MS) and nuclear magnetic resonance spectroscopy, indicated that the NREL cracked tar contained significant levels of aromatics, only slightly reduced levels from those seen in the BCL gasification tars. The two NREL whole-wood oils used in this test were analyzed by GC/MS, though no PAHs were noted. However, these samples are undergoing reanalysis specifically for PAHs at a lower detection limit.

Conclusions

John Butala, the consultant for this project, believes there was nothing discovered in this testing which constituted an unacceptable toxicity hazard for primary pyrolysis oils. These materials can be handled safely on a routine basis with commonly used safe work practices, including the use of readily available personal protective equipment. This equipment includes safety glasses or goggles, gloves, and shielding clothes.

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SPECIFICATIONS FOR LIQUID FUELS IN BOILERS

WITH CONSIDERATIONS FOR BIOMASS PYROLYSIS OILS

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ABSTRACT

The wide variety of liquid fuels currently being used in utility and industrial boilers around the world require the atomizer/burner manufacturer to develop liquid fuel specifications in order to guarantee performance. This paper discusses the relevant specifications for liquid fuels and how they affect combustion and emissions performance in industrial and utility boilers. Liquid fuel combustion issues such as atomization, stability, and heat transfer are related back to the liquid fuel's chemical composition and physical characteristics. The various affects of physical characteristics such as viscosity, heating value, pour and flash points indicate how the fuel is handled, stored and what safety concerns are warranted up to the burner. The fuel's surface tension, viscosity, density and distillation characteristics affect the atomization and evaporation process and drive the designs of industrial atomizers. With the ever increasing concern and regulations on emissions from combustion, the chemical properties and pollutant reaction kinetics of liquid fuels are becoming the driving force for fuel choice in boilers. Emissions of concern such as nitrogen and sulfur oxides, soot, particulates, and volatile organic compounds are discussed in relation to liquid fuel specifications. These parameters are addressed and attention is given to the relevant issues for biomass pyrolysis oil usage in industrial and utility boilers.

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INTRODUCTION

Liquid fuels represent an important fraction of total energy usage for industrial steam generation, process heaters and utility power generation even with the current domination of natural gas. In cases were natural gas is the primary fuel of choice, backup liquid fuel capability is critical for areas that have periods during winter where natural gas is not available or the process demands an uninteruptible source of energy. Petroleum based distillate oils and residual oils dominate the current industrial and utility liquid fuel market. However, efforts to reduce energy costs and increase plant efficiency have forced many industrial operations to consider the use of alternate fuels. Such alternative fuels include coal/water slurries, coal/oil slurries, bitumen/water emulsions, and many other fuel options linked to the specific industry which utilize a waste product for energy including biomass fuels such as sander dust, corn cobs, seed shells, etc. This wide variation in the types of fuels considered for boilers gives the impression that as long as it burns, it should be considered a suitable fuel for boilers. This is only true as long as the liquid fuel has predictable combustion properties, acceptable emissions levels, and is economically feasible. Desirable combustion properties are defined by the boiler/burner manufacturer to provide safe, consistent characteristics and efficient operation that does not cause durability problems. In the current environmental climate, local emissions regulations represent a critical, and usually dominant factor for liquid fuel choice.

BACKGROUND

The most prevalent liquid fuels used today for industrial and utility steam generation are diesel and residual oils. Diesel oil, ASTM No. 2, has relatively low amounts of fuel nitrogen and sulfur and does not require heating for pumping and atomization. Hence, diesel oil is commonly used in areas where NOx emission regulations are strict. Heavy oil, also called Bunker C or ASTM No. 6, has been used instead of the lighter more highly refined grades used for transportation, domestic and institutional heating, etc., due to its lower cost. As modern refining processes have improved the yield of the more valuable lighter grades, "straight run" or "virgin" #6 oil has become less common, and has been recreated by blending to meet accepted specifications. To understand this better, a brief review of the refining process is in order.

Modern Refining: Overview

Crude oil from the earth consists of a mixture of hydrocarbons, ranging from light, volatile gasolines and naphtha to heavy asphalt and wax. The heavier fractions are generally longer chain hydrocarbons, with higher mass ratios of carbon to hydrogen than the lighter fractions.[1]

Very simply, in a refinery the crude is heated in a furnace and separated into fractions (light to heavy) by distillation. Some remains in a gaseous phase, and is generally burned as fuel in the refinery. After the lighter fractions (gasoline, naphtha, kerosene, No. 2 oil) are removed, a black tarry residue remains, called residual or reduced crude.

Fuel Oil Specifications: Existing Standards

The most common specification currently in use in the U.S. is "ASTM D 396-92, Standard Specification for Fuel Oils" . A copy is included as Appendix I. Another common specification is "VV-F-815C", Federal Specification, Fuel Oil, Burner". These two specs are essentially identical, with the ASTM document more frequently used.[2]

To quote this widely used ASTM document, section 1.2, "This specification is for the use of purchasing agencies in formulating specifications to be included in contracts for purchases of fuel oils and for the guidance of consumers of fuel oils in the selection of the grades most suitable for their needs." This purpose is well served by this brief, very useful document, and can be included as a basis as appropriate in any purchasing or technical document.

ASTM D 396-92 requires that the fuel oil consist of petroleum derived products, and defines two general classifications, distillates and residuals, the products of the distillation process as described previously. The Appendix further categorizes and specifies oil grades No. 1, 2, 4, 5 (light), 5 (heavy), 6 ("Bunker C") and "Residual fuel oil supplied to meet regulations requiring low sulfur content . . . " The Appendix also contains an excellent discussion of the test methods used to establish relevant properties.

In addition to the properties discussed in the standard specifications, there are several other oil properties that need to be identified, understood, quantified, limited, etc., because they impact storage, handling, combustion, corrosion, and stack emissions in various degrees. The next section is a discussion of oil properties that should be understood and addressed in some manner in a complete fuel oil specification.

Fuel Oil Properties to be Understood and Specified

Generally, the physical properties of fuel oil are most important to the user, and are more commonly measured and specified. An ultimate chemical analysis is also important so that non-hydrocarbon elements and impurities such as nitrogen, sulfur, and ash, (containing metals) are quantified. Following are definitions and brief discussions on important properties.

1. **Ultimate chemical analysis**. The ultimate chemical analysis lists the weight percentages of all the chemical elements in the oil. The carbon and hydrogen percents are needed for accurate combustion calculations. The quantities of other elements and components are needed as follows:

It is important to know the composition of the ash, especially the sodium and vanadium amounts. Vanadium pentoxide and some sodium / vanadium complexes have relatively low melting temperatures, and are very corrosive in the liquid state. They can cause serious problems with heat transfer surfaces, and premature refractory failure.

Table I: Fuel Element Composition Emissions Affects

Element/Compound	Needed For
Nitrogen	NO_X Calculation
Sulfur	SO_X Calculation Particulate Calculation Corrosion and Fouling
Ash	Particulate Calculation Corrosion and Fouling

2. **Gravity**. The gravity of a fuel oil is a measure of its density. It may be indicative of its grade and heating value, and is found by using a standard hydrometer and correcting the reading at the observed temperature to the gravity at 15.6°C (60°F). The gravity scale used in the petroleum industry is the API scale, not specific gravity. They are related as follows:

$$\text{API gravity degrees} = \frac{141.5}{\text{s.g. at } 15.6^{\circ}\text{C}/15.6^{\circ}\text{C}} - 131.5 \qquad (1)$$

3. **Heating value**. There are two specified heating values for any oil, the gross (or high) heating value and the net (or low) heating value. Gross heating value includes the latent heat of evaporation of the water vapor formed during combustion, while net heating value does not. For petroleum derived fuel oils, gross heating values are higher than net heating values by about 6%, depending upon the carbon/hydrogen ratio. Gross heating value generally is used in buying and selling fuel oil. Net heating value, indicative of the usable heat produced during combustion, is used for combustion calculations.

4. **Viscosity**. Viscosity is the relative measure of an oil's resistance to flow. Quantitatively, it is the time in seconds that it takes a given amount of oil to flow through a standard-size orifice at standard temperature.[3] The Saybolt viscometer is the instrument generally used for determining the viscosity of fuel oils in the U.S. petroleum industry, and the results are expressed in Seconds Saybolt Universal SSU (sometimes SUS). For higher viscosity liquids, Seconds Saybolt Furol (SSF) is sometimes used. The use of absolute and kinematic viscosity, expressed in centipoise (cp) and centistokes (cs) respectively, are also common, especially for the lighter distillates. When evaluating a viscosity, the type of instrument and temperature must be stated. Frequently, the viscosities of No. 4, No. 5, No. 6 oils are measured by one method and it is necessary to convert to another. This is simplified by the use of conversion tables or graphs, which can be found in references 1 and 3.

Since viscosity is a measure of flow characteristics, it is an important factor in the design and operation of oil-handling and burning equipment. The efficiency and sizing of pumps, pumping

temperatures, pipeline sizing, and atomizer selection are affected by viscosity. There is also a well understood effect of liquid viscosity on drop size with increasing viscosity yielding increased drop sizes.[4] Distillate oils have low viscosities and present few problems in handling and burning. By contrast, the range of viscosities for the heavy oils is quite broad: No. 5 extends from 150 to 750 SSU at 38°C (100°F); No. 6 from 900 to 9000 SSU at 38°C (100°F). Most petroleum based oils exhibit a similar viscosity/temperature relationship.

5. **Pour Point**. The pour point of an oil is the lowest temperature at which it flows under normal conditions. In a controlled laboratory environment the pour point is 2.8°C (5°F) above the solidification temperature. Pour point is influenced substantially by the wax content, with more wax raising the pour point. The standard pour-point test, however, is only one indication of what can be expected in actual service because of the many other variables that affect the handling, storage, and use of fuel oils, such as tank size, pipeline size, oil pressure, and the structure of the wax crystals when solidifying.

Modern refining processes usually produce distillate oils that will pour freely above -12°C (10°F). Between -18 and -12°C (0 and 10°F) some wax may congeal, but it does not adversely affect system operation unless the oil has remained stationary for a long period. At temperatures below -18°C (0°F), consideration should be given to the use of a pour-point depressant. Pour points for most heavy oils typically range from -4 to 18°C (25 to 65°F). Normal heating of storage tanks, pipelines, and pumping equipment to lower viscosity keeps the oil well above this range of temperatures. For oils with a high wax or paraffin content, pour points can be as high as 52°C (125°F), and these oils present a storage and handling problem. High wax oils can change from a fluid to a solid, grease-like consistency with a temperature drop of only a few degrees due to crystallization.

6. **Flash point and fire point**. Flash point is the lowest temperature at which vapors from heated oil flash when exposed to an ignited open flame. If the heating continues, sufficient vapors are driven off to produce continuous burning for at least 5 seconds. The temperature at which this latter phenomenon occurs is called the fire point. Flash point is important because it is a measure of the oil's volatility, and indicates the maximum temperature for safe handling. Results of a flash-point test depend on the apparatus, so this is specified as well as the temperature. Distillate oils normally have flash points from 63 to 93°C (145 to 200°F), while the flash points for the heavy oils can be as high as 121°C (250°F). Thus, fuel oils do not present a fire hazard at ambient temperatures unless they are blended with a highly volatile product.

7. **Sulfur content**. The sulfur content of fuel oil has a definite relationship to the sulfur content of the crude oil from which it was refined. High sulfur crude produces high sulfur fuel oils. The different grades of fuel oils have varying percentages of sulfur, ranging from about 0.3% to 3% by weight. Distillates usually are at the lower end of the range, and residual fuels generally at the upper end. Depending on crude composition, however, it is possible for a distillate to contain more sulfur than some residuals. In combustion, many tests have shown that approximately 98% of the sulfur is oxidized to SO_2, a gas emitted to the atmosphere. The remaining 2% is oxidized to SO_3, which is a solid at ambient temperatures and contributes to particulate emissions and surface corrosion in boilers.

8. **Nitrogen content**. Crude oil also contains varying amounts of nitrogen, molecularly bound to hydrocarbon molecules. Fuel bound nitrogen content of distillate oil ranges from 0.01 to 0.10 percent by weight, and for residual ranges from 0.25 to 0.60% typically. In combustion, some of the fuel bound nitrogen (FBN) oxidizes to oxides of nitrogen (NO_x), with the remainder recombining to form N_2. The conversion rate to NO_x is very high for distillates with low FBN, and decreases as the FBN increases. In all cases, a higher FBN content produces more total NO_x.[5]

9. **Ash**. The ash content of a fuel oil is the residue, excluding carbon, remaining after combustion at a specified high temperature. The ash results from a variety of inorganic and metal-containing compounds present in the crude oil, catalyst fines from cracking, contaminants acquired during transportation and storage, and from additives which are used to improve particular fuel properties. Ash generally passes through the combustion process and out the stack as particulate matter. Some of the ash fouls the heat transfer surfaces if it is heated to its melting or softening point. The actual composition of the ash is needed to evaluate fouling and high temperature corrosion potential. This is done by spectrographic analysis. Catalyst fines (particles of silica alumina) are erosive to pumps and atomizers. They will settle out in storage tanks. Efficient filtration is necessary to protect equipment.

10. **Bottom sediment and water (BSW)**. Water and sediment are contaminants found in all grades of fuel oil. The total amount of water and sediment usually is determined by a centrifuge test. An extraction method is used to determine sediment by itself; distillation to find the amount of water. Distillate oils have only from a trace to 0.2% of water and sediment; the heavier grades have from 0.1% to 2%. Generally, BSW should not exceed 1.0%.

11. **Carbon residue**. The carbon residue of a petroleum product is the amount of carbonaceous residue remaining after evaporation and pyrolysis of that product.[6] When an oil is evaporated, free carbon remains either because it was originally present, or because it was formed by cracking during the evaporation process. The amount of carbon remaining depends on the type of oil and indicates to some extent the tendency of the oil to carbonize on burner nozzles. High levels of carbon residue may also cause an increase in particulate emissions in small furnaces with short residence times, especially when poorly atomized (large droplets) for combustion.

Carbon residue is measured either by the Conradson test with an open flame or the Ramsbottom test with heat applied through a molten bath. Formulas are available for converting the results from one test to the equivalent value of the other test. A relatively new carbon residue parameter, called the Coke Formation Index (CFI), is experimentally determined by careful burning of single fuel droplets yielding a more realistic measurement of the coke forming potential of the fuel oil.[7] The CFI is approximately 50% of the Conradson Carbon Residue. These single droplet experimental tests have yielded a relationship between the initial droplet diameter and the resulting coke particle diameter as shown in the following equation[7]

$$CFI = 6\frac{D_c^2}{D_o^3}\frac{\rho_c \tau}{\rho_o} \tag{2}$$

where D is diameter, ρ is the density, τ is the coke particle shell thickness and the subscripts c and o represent coke and oil, respectively. The diameter ratio term is taken to be constant as well as the product of the coke particle density and shell thickness. This allows a direct calculation of the coke particle diameter from the initial droplet diameter. Given an assumed initial droplet distribution, equation 2 is used to calculate the coke particle diameters for two values of CFI, as shown in Figure 1. This information on coke particle diameter is used with a simple Ahhrenius oxidation relationship for coke particles assuming constant particle density and shrinking particle diameter to determine the percentage of coke particle burnout for each coke particle diameter, as shown in Figure 2. The importance of reducing the particle diameter is shown in Figure 3 where the initial droplet diameter volume fraction is compared to the coke particle mass fraction for each of the assumed diameter ranges. The coke particles present in the flue gas result from the larger droplet diameters in the spray.

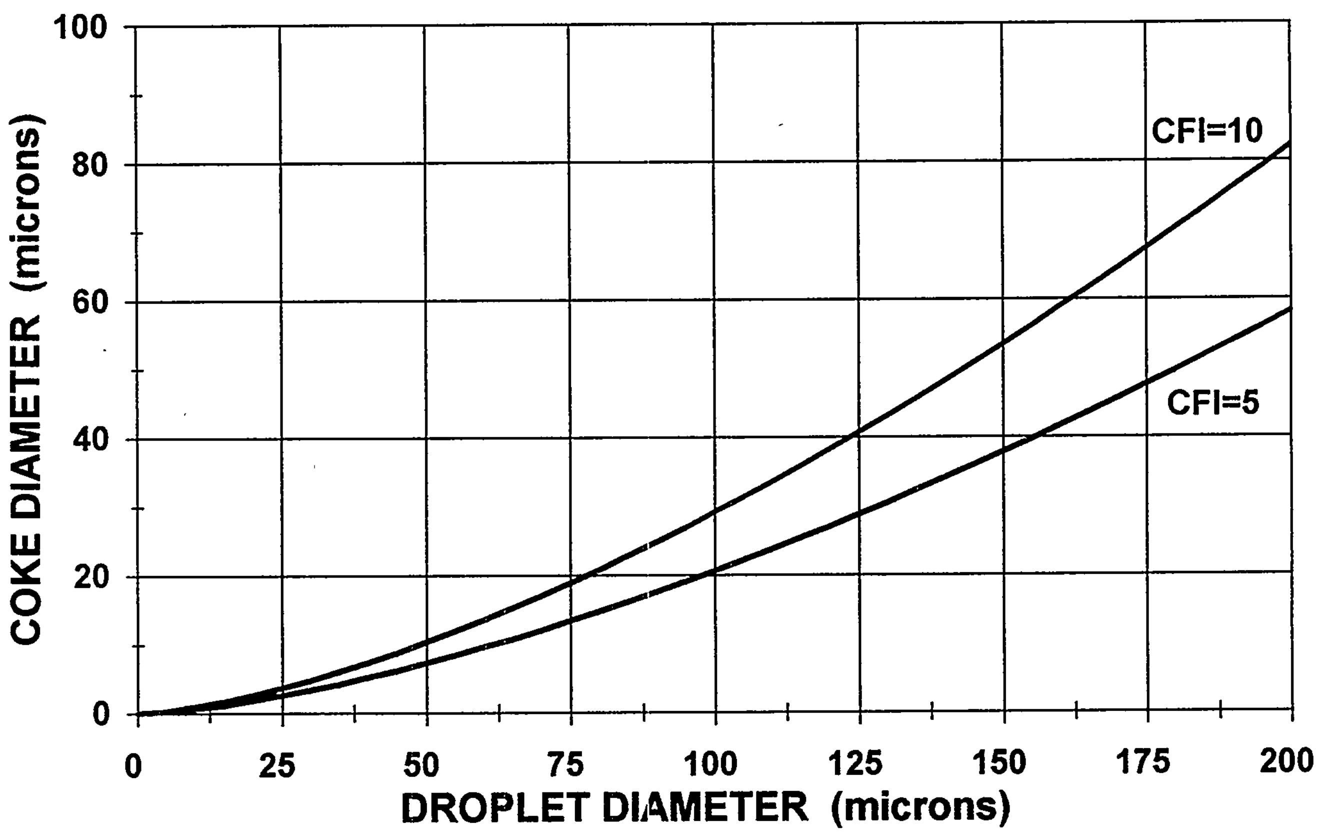

Figure 1: Coke particle diameters resulting from initial droplet size using the Coke Formation Index. (Urban and Dryer, 1990)

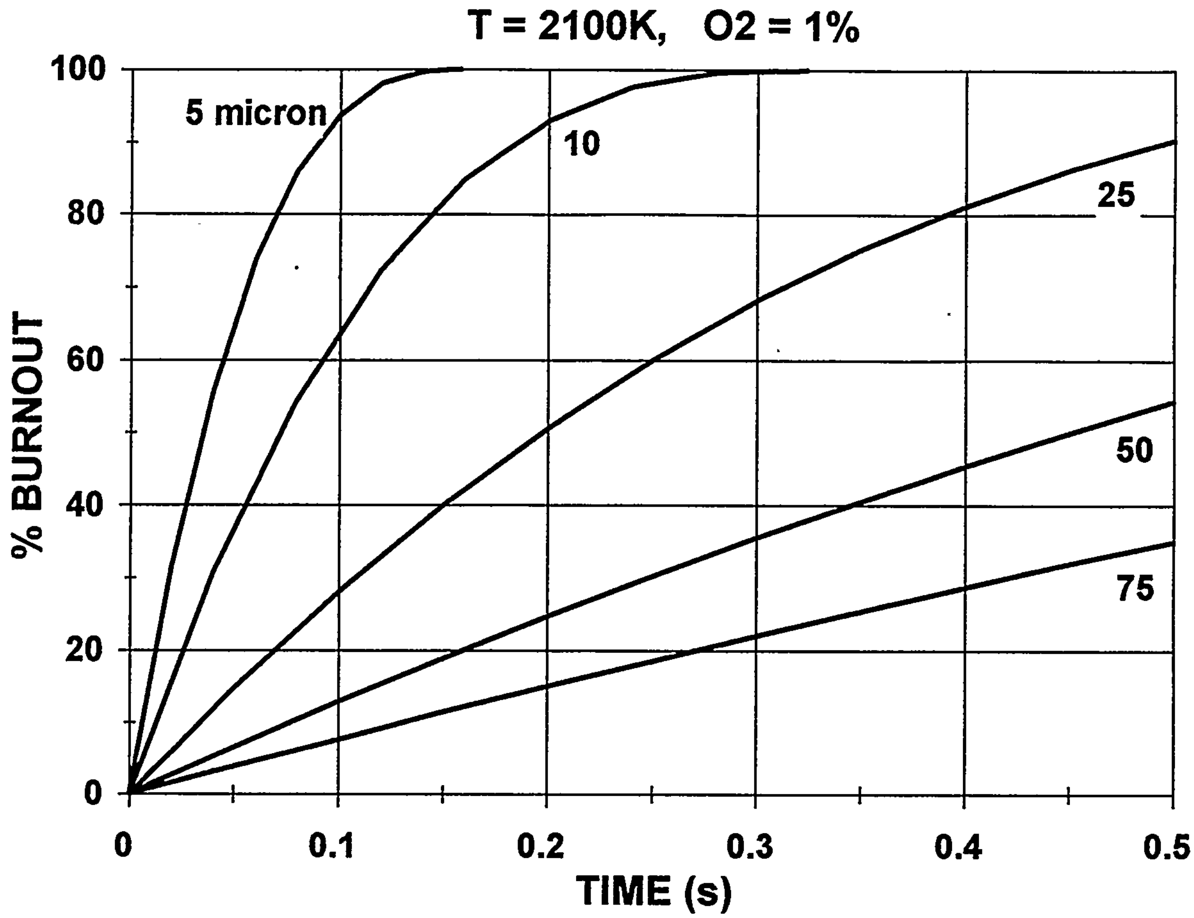

Figure 2: Relationship of coke particle diameter to percentage burnout for fixed combustion environment.

12. **Distillation curve**. A distillation test establishes the quantity and number of fractions which make up a liquid fuel. This test is only applicable to distillate oils. The test is performed by heating the sample and condensing the vapor. The temperatures are recorded for successive volume percentages distilled. This is continued until all of the sample has been distilled or until boiling ceases at the final temperature.

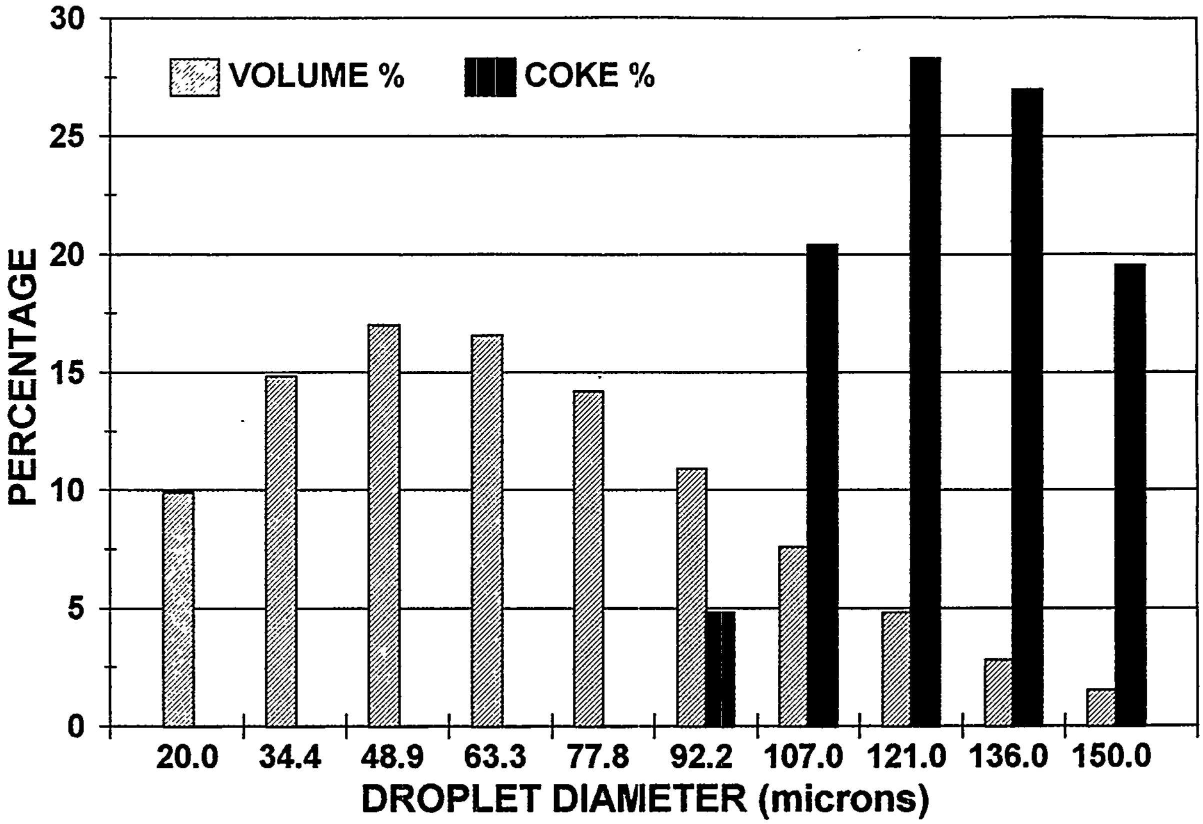

Figure 3: Histogram of droplet diameters and resulting coke particle diameters.

BIOMASS PYROLYSIS OILS

Biomass pyrolysis oils are created when a biomass feed stock is heated without oxygen until the feed stock pyrolyzes and vapors are given off. The heavier hydrocarbon vapors are collected and condensed to form an oil that has specific properties. There are many physical and chemical differences between biomass pyrolysis oils and the petroleum derived oils previously mentioned.

Petroleum based distillates typically have specific gravities less than unity and residual oils of about unity. The biomass pyrolysis oils are heavier than water with specific gravities up to 1.2 while having a higher heating value of about 50% that of typical petroleum fuels. These oils have a large amount of free water which is another distinct difference between typical petroleum derived fuels. Another interesting characteristic of pyrolysis oils is that some have viscosities at room temperature that are too high to produce a finely atomized spray with current industrial atomizer designs.

Biomass pyrolysis oils also have vastly different chemical composition than petroleum fuels with increased levels of carbon-to-hydrogen ratio, increased fuel oxygen, and alkali components. The fuel nitrogen levels exceed those for diesel oils but are on par with many residual oils. The sulfur content of biomass pyrolysis oils are close to a typical diesel oil and less than most residual oils.

The distillation characteristics for biomass pyrolysis oils are also quite different from petroleum derived oils. The initial boiling point for biomass pyrolysis oils occurs near the boiling point of water due to the high level of water in the fuel. The final boiling point of these fuels is typically less than 400°F which is below the initial boiling point for many of the heavier grades of petroleum based fuels. A startling feature of biomass pyrolysis oils is the residue left after distillation. The distillation residue can be as high as 48% compared with a maximum residue of approximately 25% for residual oils with high asphaltene concentrations.

Potential Problem Areas with Biomass Pyrolysis Oil Combustion

The following will summarize common problem areas that can be expected with biomass pyrolysis oils that have specific undesirable properties. Cognizance of them will help in explaining or avoiding certain operational problems.

1. **Atomization quality**. The droplet size distribution and spray shape are critical parameters for evaluating spray combustion. Typically, the goals are to provide a sufficiently fine fuel spray to promote evaporation and mixing with air and recirculation patterns to provide suitable stability and fuel burnout. The spray shape is used very simply to fill the furnace with the flame without allowing liquid fuel to impinge on boiler tube or refractory walls where carbon deposits and corrosion can occur. Many factors affect droplet size from industrial fuel atomizers yet the most salient to biomass pyrolysis oils are viscosity and surface tension. Increased fuel viscosity and surface tension result in sprays with larger drop sizes with all other factors held constant. Biomass pyrolysis oils to be burned must have viscosities of less than 150 SSU for proper atomization without excessive atomizing media consumption, steam or air. The surface tension of a fuel dictates the liquid's resistance to being broken apart. Petroleum based fuels all have relatively low surface tensions when at the desired atomization viscosity. Due to the high water content of biomass pyrolysis oils with its high surface tension, the resulting drop sizes may be much larger than would be obtained with similar conditions on a petroleum fuel.

2. **NO_X**. Nitrogen oxides (NO_X) are by far the most regulated pollutant emission from industrial and utility combustion systems. The sources for NO_X in combustion systems are separated into thermal, prompt or fuel NO_X. Thermal NO_X is highly dependent upon flame temperature and is formed via the extended Zeldovich mechanism when atmospheric nitrogen dissociates and the resulting molecular nitrogen attached to a free oxygen atom. Prompt NO_X is formed early on in the combustion process through hydrocarbon radicals. Fuel NO_X is formed when the fuel contains molecular nitrogen that oxidizes in the flame. The most common technique for minimizing NO_X emissions from combustion systems is to stage the combustion into rich and lean regimes to reduce flame temperatures and available oxygen.

The water content in biomass pyrolysis oils and their low heating value can combine to reduce flame temperatures and result in a reduction in thermal NO_X production. However, the fuel nitrogen present in biomass pyrolysis oils has great potential for forming fuel NO_X. This problem is exacerbated when considering the high oxygen concentrations in the fuel itself. This high fuel oxygen concentration can impede the effectiveness of operation at reduced excess oxygen to reduce FBN conversion to NO_X.

3. **Heating value.** The low heating value of biomass pyrolysis oils causes a design problem. Piping, pumping and atomizer designs are driven by the heating value of the fuel to be used. It will be difficult to design a system that can operate effectively over a wide turn down range with both petroleum based fuels and biomass pyrolysis oils which will require approximately twice the volume flow rate for the same heating load. This increase liquid flow rate requires the need for an atomizer designed specifically for the biomass pyrolysis oil.

4. **Coke particulate**. The high residual carbon content of biomass pyrolysis oils combined with the low heating value and high water content will undoubtedly lead to increased coke particulate formation and emission. The formation of these coke particles is quite composition dependent and should be investigated further. It is also important to evaluate the oxidation kinetics of biomass pyrolysis oil coke particles for comparison to petroleum fuels.

5. **Asphaltenes**. Asphaltenes (very high molecular weight, long chain hydrocarbons) and wax are not detected with normal test methods, because the solvents used, benzol and toluene, dissolve them. The presence of these compounds usually is not detected until they cause problems. Heat can eliminate wax, but asphaltenes require a solvent for dissolution, and this generally is impractical in a fuel oil system. Asphaltenes tend to cause excessive carbon formation on burner tips. Fuels with high wax content are prone to plugging unless sufficiently heated.

6. **Thermally unstable oils**. Biomass pyrolysis oils are quite thermally unstable. This will cause distinct problems when using an oil that has a higher viscosity at room temperature than 150 SSU. Typically, residual oils are heated (up to 200°F) until the viscosity is reduced to the point that proper atomization can be achieved. Heating of a pyrolysis oil to these temperatures can cause thermal breakdown of the oil and cause coking inside of pipelines and the atomizer. Burner tip and strainer plugging result from unstable oil blends that cause asphaltene precipitation and polymer formation. Another problem could be vapor lock or increased atomizing pressures due to heating the fuel near the initial boiling point.

7. **Low initial boiling point**. Perhaps the most common type of atomizing fluid used in industrial atomizers is steam. This steam is typically at a temperature exceeding 200°F which can cause the lighter hydrocarbons to flash once emitted from the atomizer. Burner pulsation can result when these low boiling fractions prematurely vaporize. These vaporized light fractions mix rapidly with fresh combustion air and are diluted near the low end of the flammability range. This can cause the stabilizing location of the spray flame to oscillate causing strong pulsations. Ignition and stability problems can occur with wide boiling range oil blends.

8. **Fuel pH.** Biomass pyrolysis oils are highly acidic and corrosive to many of the materials that make up fuel storage and delivery systems and atomizer components. Another issue of potential concern is the safety of workers that may/will be exposed to spills and leaks.

9. **Akali components.** Biomass pyrolysis oils have much greater amounts of alkali components than typical petroleum oils. These alkali components have the potential to form acids that could cause boiler tube erosion if allowed to condense. They also have the capability to form particles that would increase the total amount of particulate emissions.

SUMMARY

The specifications for liquid fuels in boilers have been introduced and defined. In addition, the chemical composition and physical properties for biomass pyrolysis oils have been presented and potential problems areas defined. The following are the salient features of this paper:

- The physical properties and chemical components of a liquid fuel are carefully considered to determine storage and handling, atomization, combustion and emissions information for boilers.
- Biomass pyrolysis oil has greatly differing chemical and physical properties than that of petroleum derived liquid fuels.
- The increased levels of free water and oxygen and decreased heating value in biomass pyrolysis oils poses an engineering challenge to develop an effective atomizer / burner system for low emissions combustion.

While there are many challenges associated with the development of biomass pyrolysis oil combustion equipment for industrial and utility steam generation, there does appear to be hope in determining the best suited application for these oils. Most industrial combustion equipment sold currently requires the evaluation of specific pollutants. The future has the potential to introduce a new parameter of interest, carbon dioxide emissions. If the environmental / economic environment changes to place a value on reduced carbon dioxide emissions, then the potential value of biomass pyrolysis oils will escalate. As this economic value increases, the engineering solutions will follow to develop acceptable combustion equipment for biomass pyrolysis oil combustion.

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An American National Standard

Standard Specification for Fuel Oils[1]

This standard is issued under the fixed designation D 396; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This specification has been approved for use by agencies of the Department of Defense to replace Fed Std VV-FF-815. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

1. Scope

1.1 This specification (Note 1) covers grades of fuel oil intended for use in various types of fuel-oil-burning equipment under various climatic and operating conditions. These grades are described as follows:

1.1.1 Grades 1 and 2 are distillate fuels for use in domestic and small industrial burners. Grade 1 is particularly adapted to vaporizing type burners or where storage conditions require low pour point fuel.

1.1.2 Grades 4 (Light) and 4 are heavy distillate fuels or distillate/residual fuel blends used in commercial/industrial burners equipped for this viscosity range.

1.1.3 Grades 5 (Light), 5 (Heavy), and 6 are residual fuels of increasing viscosity and boiling range, used in industrial burners. Preheating is usually required for handling and proper atomization.

NOTE 1—For information on the significance of the terminology and test methods used in this specification, see Appendix X1.

NOTE 2—A more detailed description of the grades of fuel oils is given in Appendix X1.3.

1.2 This specification is for the use of purchasing agencies in formulating specifications to be included in contracts for purchases of fuel oils and for the guidance of consumers of fuel oils in the selection of the grades most suitable for their needs.

1.3 Nothing in this specification shall preclude observance of federal, state, or local regulations which can be more restrictive.

1.4 All values are stated in SI units and are regarded as standard.

NOTE 3—The generation and dissipation of static electricity can create problems in the handling of distillate burner fuel oils. For more information on the subject, see Guide D 4865.

2. Referenced Documents

2.1 *ASTM Standards:*

D 56 Test Method for Flash Point by Tag Closed Tester[2]
D 86 Test Method for Distillation of Petroleum Products[2]
D 93 Test Methods for Flash Point by Pensky-Martens Closed Tester[2]
D 95 Test Method for Water in Petroleum Products and Bituminous Materials by Distillation[2]
D 97 Test Method for Pour Point of Petroleum Oils[2]
D 129 Test Method for Sulfur in Petroleum Products (General Bomb Method)[2]
D 130 Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test[2]
D 445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)[2]
D 473 Test Method for Sediment in Crude Oils and Fuel Oils by the Extraction Method[2]
D 482 Test Method for Ash from Petroleum Products[2]
D 524 Test Method for Ramsbottom Carbon Residue of Petroleum Products[2]
D 1266 Test Method for Sulfur in Petroleum Products (Lamp Method)[2]
D 1298 Practice for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method[2]
D 1552 Test Method for Sulfur in Petroleum Products (High-Temperature Method)[2]
D 1796 Test Method for Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure)[2]
D 2622 Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry[3]
D 3245 Test Method for Pumpability of Industrial Fuel Oils[3]
D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter[3]
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[3]
D 4294 Test Method for Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectrometry[3]
D 4865 Guide for Generation and Dissipation of Static Electricity in Petroleum Fuel Systems[4]

3. General Requirements

3.1 The grades of fuel oil specified herein shall be homogeneous hydrocarbon oils, free from inorganic acid, and free from excessive amounts of solid or fibrous foreign matter.

3.2 All grades containing residual components shall remain uniform in normal storage and not separate by gravity

[1] This specification is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.E on Burner, Diesel, and Gas Turbine Fuel Oils.

Current edition approved Oct. 15, 1992. Published December 1992. Originally published as D 396 – 34 T. Last previous edition D 396 – 90a.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 05.02.

[4] *Annual Book of ASTM Standards*, Vol 05.03.

TABLE 1 Detailed Requirements for Fuel Oils[A]

Property	ASTM Test Method[B]	No. 1	No. 2	Grade No. 4 (Light)	No. 4	No. 5 (Light)	No. 5 (Heavy)	No. 6
Flash Point °C, min	D 93	38	38	38	55	55	55	60
Water and sediment, % vol, max	D 1796	0.05	0.05	(0.50)[C]	(0.50)[C]	(1.00)[C]	(1.00)[C]	(2.00)[C]
Distillation temperature °C	D 86							
10 % vol recovered, max		215	...	...	...	...	...	...
90 % vol recovered, min		...	282	...	...	...	...	...
max		288	338	...	...	...	...	...
Kinematic viscosity at 40°C, mm²/s	D 445							
min		1.3	1.9	1.9	>5.5	...	...	...
max		2.1	3.4	5.5	24.0[D]			
Kinematic viscosity at 100°C, mm³/s								
min		...	...	...	...	5.0	9.0	15.0
max		...	...	...	...	8.9[D]	14.9[D]	50.0[D]
Ramsbottom carbon residue on 10 % distillation residue % mass, max	D 524	0.15	0.35	...	...	...	...	...
Ash, % mass, max	D 482	...	...	0.05	0.10	0.15	0.15	...
Sulfur, % mass max[E]	D 129	0.50	0.50	...	...	...	...	...
Copper strip corrosion rating, max, 3 h at 50°C	D 130	No. 3	No. 3	...	...	...	...	...
Density at 15°C, kg/m³	D 1298							
min		...	...	>876[F]	...	...	...	...
max		850	876	...	...	...	...	...
Pour Point °C, max[G]	D 97	− 18	−6	−6	−6	...	...	[H]

[A] It is the intent of these classifications that failure to meet any requirement of a given grade does not automatically place an oil in the next lower grade unless in fact it meets all requirements of the lower grade. However, to meet special operating conditions modifications of individual limiting requirements may be agreed upon among the purchaser, seller and manufacturer.

[B] The test methods indicated are the approved referee methods. Other acceptable methods are indicated in Section 2 and 5.1.

[C] The amount of water by distillation by Test Method D 95 plus the sediment by extraction by Test Method D 473 shall not exceed the value shown in the table. For Grade No. 6 fuel oil, the amount of sediment by extraction shall not exceed 0.50 mass %, and a deduction in quantity shall be made for all water and sediment in excess of 1.0 mass %.

[D] Where low sulfur fuel oil is required, fuel oil falling in the viscosity range of a lower numbered grade down to and including No. 4 can be supplied by agreement between the purchaser and supplier. The viscosity range of the initial shipment shall be identified and advance notice shall be required when changing from one viscosity range to another. This notice shall be in sufficient time to permit the user to make the necessary adjustments.

[E] Other sulfure limits may apply in selected areas in the United States and in other countries.

[F] This limit assures a minimum heating value and also prevents misrepresentation and misapplication of this product as Grade No. 2.

[G] Lower or higher pour points can be specified whenever required by conditions of storage or use. When a pour point less than −18°C is specified, the minimum viscosity at 40°C for grade No. 2 shall be 1.7 mm²/s and the minimum 90 % recovered temperature shall be waived.

[H] Where low sulfur fuel oil is required, Grade No. 6 fuel oil will be classified as Low Pour (+15°C max) or High Pour (no max). Low Pour fuel oil should be used unless tanks and lines are heated.

into light and heavy oil components outside the viscosity limits for the grade.

4. Detailed Requirements

4.1 The various grades of fuel oil shall conform to the limiting requirements shown in Table 1. A representative sample shall be taken for testing in accordance with Practice D 4057.

4.2 Modifications of limiting requirements to meet special operating conditions agreed upon between the purchaser, the seller, and the supplier shall fall within limits specified for each grade, except as stated in supplementary footnotes for Table 1.

5. Test Methods

5.1 The requirements enumerated in this specification shall be determined in accordance with the following ASTM test methods,[5] except as may be required under 5.1.1.

5.1.1 *Flash Point*—Test Methods D 93, except where other methods are prescribed by law for the determination of minimum flash point. For Grades No. 1 and No. 2, Test Method D 56 can be used as an alternative with the same limits, provided the flash point is below 79.4°C and the viscosity is below 5.8 cSt at 38°C. This test method will give slightly lower values. In cases of dispute, Test Methods D 93 shall be used as the referee method.

5.1.2 *Pour Point*—Test Method D 97. Alternative test methods that indicate flow point properties can be used for low sulfur residual fuels by agreement between purchaser and supplier.

5.1.3 *Water and Sediment*—The water and sediment in Grades Nos. 1 and 2 shall be determined in accordance with Test Method D 1796 and in Grade Nos. 4, 5, and 6 by Test Method D 95, and Test Method D 473. A density of 1.0 kg/L shall be used for the Test Method D 95 water.

5.1.4 *Carbon Residue*—Test Method D 524.

5.1.5 *Ash*—Test Method D 482.

5.1.6 *Distillation*—Distillation of Grade No. 1 and No. 2 oils shall be determined in accordance with Test Method D 86.

5.1.7 *Viscosity*—Viscosity shall be determined in accordance with Test Method D 445.

5.1.8 *Density*—Practice D 1298. Test Method D 4052 can be used as an alternate with the same limits. In case of dispute, Practice D 1298 shall be used as the referee method.

5.1.9 *Corrosion*—Test Method D 130, 3 h test at 50°C.

5.1.10 *Sulfur*—Test Method D 129. Test Methods D 1552, D 2622, and D 4294 can also be used for all grades.

[5] For information on the precision of the ASTM test methods for fuel oils refer to "An Evaluation of Methods for Determination of Sulfur in Fuel Oils" by A. R. Crawford, Esso Mathematics & Systems Inc. and G. V. Dyroff, Esso Research and Engineering Co., 1969. This document is available from the Publications Section, American Petroleum Institute, 2101 L St., N.W., Washington, DC 20037.

In addition, Test Method D 1266 can be used for Grade 1, but only with samples having sulfur contents of 0.4 mass per cent and less (down to 0.01 %). In case of dispute, Test Method D 129 is the referee test method for this specification.

6. Keywords

6.1 burner fuels; fuel oils; furnace oils: petroleum and petroleum products; specifications

APPENDIX

(Nonmandatory Information)

X1. SIGNIFICANCE OF ASTM SPECIFICATION FOR FUEL OILS

X1.1 Scope

X1.1.1 This specification divides fuel oils into grades based upon the types of burners for which they are suitable. It places limiting values on several of the properties of the oils in each grade. The properties selected for limitation are those that are believed to be of the greatest significance in determining the performance characteristics of the oils in the types of burners in which they are most commonly used.

X1.2 Classes

X1.2.1 Because of the methods employed in their production, fuel oils fall into two broad classifications: distillates and residuals. The distillates consist of overhead or distilled fractions. The residuals are bottoms remaining from the distillation, or blends of these bottoms with distillates. In this specification, Grades No. 1 and No. 2 are distillates and the grades from No. 4 to No. 6 are usually residual, although some heavy distillates can be sold as Grade No. 4.

X1.3 Grades

X1.3.1 *Grade No. 1* is a light distillate intended for use in burners of the vaporizing type in which the oil is converted to a vapor by contact with a heated surface or by radiation. High volatility is necessary to ensure that evaporation proceeds with a minimum of residue.

X1.3.2 *Grade No. 2* is a heavier distillate than grade No. 1. It is intended for use in atomizing type burners which spray the oil into a combustion chamber where the tiny droplets burn while in suspension. This grade of oil is used in most domestic burners and in many medium capacity commercial-industrial burners where its ease of handling and ready availability sometimes justify its higher cost over the residual fuels.

X1.3.3 *Grade No. 4 (Light)* is a heavy distillate fuel or distillate/residual fuel blend meeting the specification viscosity range. It is intended for use both in pressure-atomizing commercial-industrial burners not requiring higher cost distillates and in burners equipped to atomize oils of higher viscosity. Its permissible viscosity range allows it to be pumped and atomized at relatively low-storage temperatures.

X1.3.4 *Grade No. 4* is usually a heavy distillate/residual fuel blend but can be a heavy distillate fuel meeting the specification viscosity range. It is intended for use in burners equipped with devices that atomize oils of higher viscosity than domestic burners can handle. Its permissible viscosity range allows it to be pumped and atomized at relatively low storage temperatures. Thus, in all but extremely cold weather it requires no preheating for handling.

X1.3.5 *Grade No. 5 (Light)* is residual fuel of intermediate viscosity for burners capable of handling fuel more viscous than grade No. 4 without preheating. Preheating can be necessary in some types of equipment for burning and in colder climates for handling.

X1.3.6 *Grade No. 5 (Heavy)* is a residual fuel more viscous than Grade No. 5 (Light) and is intended for use in similar service. Preheating may be necessary in some types of equipment for burning and in colder climates for handling.

X1.3.7 *Grade No. 6,* sometimes referred to as Bunker C, is a high-viscosity oil used mostly in commercial and industrial heating. It requires preheating in the storage tank to permit pumping, and additional preheating at the burner to permit atomizing. The extra equipment and maintenance required to handle this fuel usually preclude its use in small installations.

X1.3.8 Residual fuel oil supplied to meet regulations requiring low sulfur content can differ from the grade previously supplied. It may be lower in viscosity (and fall into a different grade number). If it must be fluid at a given temperature, Test Method D 97 need not accurately reflect the pour point which can be expected after a period of storage. It is suggested that the purchaser and supplier discuss the proper handling and operating techniques for a given low-sulfur residual fuel oil in the installation where it is to be used.

X1.4 Significance of Test Methods

X1.4.1 The significance of the properties of fuel oil on which limitations are placed by the specification is as follows:

X1.4.1.1 *Flash Point*—The flash point of a fuel oil is an indication of the maximum temperature at which it can be stored and handled without serious fire hazard. The minimum permissible flash point is usually regulated by federal, state, or municipal laws and is based on accepted practice in handling and use.

X1.4.1.2 *Pour Point*—The pour point is an indication of the lowest temperature at which a fuel oil can be stored and still be capable of flowing under very low forces. The pour point is prescribed in accordance with the conditions of storage and use. Higher pour point fuels are permissible where heated storage and adequate piping facilities are provided. An increase in pour point can occur when residual fuel oils are subjected to cyclic temperature variations that can occur in the course of storage or when the fuel is preheated and returned to storage tanks. To predict these properties, Test Method D 3245 may be required.

X1.4.1.3 *Water and Sediment*—Appreciable amounts of water and sediment in a fuel oil tend to cause fouling of

facilities for handling it, and to give trouble in burner mechanisms. Sediment may accumulate in storage tanks and on filter screens or burner parts, resulting in obstruction to flow of oil from the tank to the burner. Water in distillate fuels can cause corrosion of tanks and equipment and it can cause emulsions in residual fuels.

X1.4.1.4 *Carbon Residue*—The carbon residue of a fuel is a measure of the carbonaceous material left after all the volatile components are varporized in the absence of air. It is a rough approximation of the tendency of a fuel to form deposits in vaporizing burners, such as pot-type and sleeve-type burners, where the fuel is vaporized in an air-deficient atmosphere.

X1.4.1.4*(1)* To obtain measurable values of carbon residue in the lighter distillate fuel oils, it is necessary to distill the oil to remove 90 % of it in accordance with Section 9 of Test Method D 524, and then determine the carbon residue concentrated in the remaining 10 % bottoms.

X1.4.1.5 *Ash*—The amount of ash is the quantity of noncombustible material in an oil. Excessive amounts can indicate the presence of materials that cause high wear of burner pumps and valves, and contribute to deposits on boiler heating surfaces.

X1.4.1.6 *Distillation*—The distillation test shows the volatility of a fuel and the ease with which it can be vaporized. The test is of greater significance for oils that are to be burned in vaporizing type burners than for the atomizing type. For example, the maximum 10 % and 90 % distilled temperatures are specified for grade No. 1 fuel. The limiting 10 % value assures easy starting in vaporizing type burners and the 90 % limit excludes heavier fractions that would be difficult to vaporize.

X1.4.1.6*(1)* The limits specified for grade No. 2 heating oil define a product that is acceptable for burners of the atomizing type in household heating installations. Distillation limits are not specified for fuel oils of grades Nos. 4, 5, and 6.

X1.4.1.7 *Viscosity Limits for Grades Nos. 1 and 2*—The viscosity of an oil is a measure of its resistance to flow. In fuel oil it is highly significant since it indicates both the relative ease with which the oil will flow or can be pumped, and the ease of atomization.

X1.4.1.7*(1)* Viscosity limits for No. 1 and No. 2 grades are specified to help maintain uniform fuel flow in appliances with gravity flow, and to provide satisfactory atomization and constant flow rate through the small nozzles of household burners. For the heavier grades of industrial and bunker fuel oils, viscosity is of major importance, so that adequate preheating facilities can be provided to permit them to be pumped to the burner and to provide good atomization. However, it is equally important that the maximum viscosity under the existing conditions be such that the oil can be pumped satisfactorily from the storage tank to the preheater.

X1.4.1.8 *Density*—Density alone is of little significance as an indication of the burning characteristics of fuel oil. However, when used in conjunction with other properties, it is of value in mass-volume relationships and in calculating the specific energy (heating value) of an oil.

X1.4.1.9 *Corrosion*—The corrosion test serves to indicate the presence or absence of materials that could corrode copper, brass, and bronze components of the fuel system. This property is specified only for Nos. 1 and 2 distillate fuel oils.

X1.4.1.10 Limited sulfur content of fuel oil can be required for special uses in connection with heat treatment, nonferrous metal, glass, and ceramic furnaces or to meet federal, state, or local legislation or regulations.

X1.4.1.11 *Nitrogen*—Nitrogen oxide emission regulations have been imposed on certain combustion facilities as a function of fuel nitrogen content. For purposes of these regulations, distillate fuels, low nitrogen residual fuels, and high nitrogen residual fuels have been defined by their nitrogen content. Installations are required to meet different emission standards according to the classification of the fuel being used. When regulations require such a distinction to be made, fuel nitrogen specifications can be needed in the contractual agreement between the purchaser and the supplier.

SPRAYS AND SPRAY COMBUSTION

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The behavior of liquid fueled combustion devices is strongly influenced by the fuel injection system, and biomass pyrolysis oil fueled systems are no exception. The purpose of the fuel injection system is to control and enhance the mixing of the fuel with oxidizer, usually the oxygen in air, which requires that the liquid be first evaporated and then mixed with the air through appropriate entrainment and diffusional pathways. An examination of liquid evaporation and mixing rates likely to be found in practical devices convinces one that atomization of the liquid into small droplets is required if the evaporation and mixing is to occur reasonably fast. Useful references for understanding sprays and spray combustion include Lefebvre [1] and Chigier [2].

Atomization

Atomization is the process of breaking liquids into small droplets. Figure 1 illustrates the atomization of a liquid jet, a liquid sheet, and a large droplet. In each case, the liquid is deformed and broken into small elements as a result of aerodynamic or viscous forces overcoming the resistance of surface tension. Important parameters include the Weber and Reynold's numbers:

$$W = \frac{\rho U^2 d}{\sigma}$$

$$R = \frac{\rho U d}{\mu}$$

where ρ is the density, U the relative velocity between air and liquid, d a characteristic length, and σ the surface tension and μ the viscosity. The Weber number represents the ratio of inertial to surface forces and the Reynolds number the ratio of inertial to viscous forces. These two numbers can be combined to form a ratio of viscous to surface forces. The resulting non-dimensional group is named the Ohnesorge number:

$$Oh = \frac{W^{1/2}}{R}$$

Consider the atomization behavior of a round jet, the simplest form of liquid fuel injection. Figure 2 illustrates the breakup regimes experienced by the jet as the jet velocity is increased relative to the surrounding air stream. These regimes are controlled by different mechanisms, of which only the full atomization regime has practical significance for combustion applications. Figure 3 shows these regimes in terms of Ohnesorge Number plotted against Reynolds number. As one can see, the criteria for full atomization is that conditions lie above a line approximately defined by the relation

$$Oh = 100R^{-0.92}$$

Typical room temperature properties of biomass pyrolysis oil and hydrocarbon fuels are shown in Table I.

	Biomass Pyrolysis Oil	Heavy Fuel Oil	Light Fuel Oil	Ethyl Alcohol	n-Octane
Viscosity (kg/msec)	200	.57	.17	.002	.0005
Surface Tension (kg/sec^2)	~.02	.023	.025	.024	.02
Density (kg/m^3)	~1000	970	930	791	700

Table II shows the range of values of W, R and Oh for the fuels of Table I for typical fuel jet conditions of 20 m/sec and 500 microns diameter.

	W	R	Oh
Biomass Pyrolysis Oil	20,000	0.05	2,828
Heavy Fuel Oil	16,870	17	7.6
Light Fuel Oil	14,880	55	2.2
Ethyl Alcohol	14,501	3,955	0.03
n-Octane	14,000	14,000	0.008

Thus biomass pyrolysis oils will be difficult to atomize, requiring special attention to this problem.

Atomizers and Atomizer Performance

Sprays can be generated a variety of ways. What is needed is a high relative velocity between the liquid to be atomized and a surrounding air stream. The relative velocity can be generated by accelerating the liquid, the air, or both. Atomizers which accelerate the liquid exclusively by pressure drop are called pressure atomizers. Example of pressure

atomizer configurations are shown in Figure 4. If the air is accelerated also the atomizer is designated as air assist or air blast, as illustrated in Figure 5. Some atomizers accelerate the liquid by mechanical means. The rotary atomizer shown in Figure 6 is an example.

The performance of an atomizer is determined by the resulting droplet size distribution. Figure 7 illustrates a normalized size distribution, as well as number and volume cumulative distributions. The distribution properties are often characterized by weighted mean diameters. Generally

$$(D_{ab})^{a-b} = \frac{\int D^a (dN / dD) dD}{\int D^b (dN / dD) dD}$$

where a and b are moment parameters. The most commonly used weighting is for a = 3 and b = 2. The resulting diameter is called the Sauter Mean Diameter and is important because it relates to the average mass transfer rate between droplets and air. Figure 8 shows the Sauter Mean Diameter for the air blast atomizer configuration in the figure as a function of liquid mass flow rate and air pressure drop.

Drop Evaporation and Burning

Once the spray is formed, the combustion characteristics will be affected by how rapidly the resulting droplets evaporate and burn. It is often observed that the droplets evaporate according to the so called "D Squared" Law:

$$D^2 = D_0^2 - Kt$$

where K is approximately constant. A more detailed analysis shows that the overall mass burning rate of the droplet is of the form

$$\dot{m} = 2\pi D_s (\frac{k}{c_p}) \ln(1+B)(1+0.3R_D^{0.5}\,\mathrm{Pr}^{0.33})$$

where R is the Reynolds number of the drop based on the relative velocity between the droplet and the surrounding gas, Pr the Prandtl number of the surrounding gas, and B the transfer number:

$$B = \frac{c_{pg}(T_f - T_b)}{L + c_{pF}(T_f - T_{F0})}$$

where T_f, T_b and T_{F0} are the flame, boiling and initial droplet temperature respectively, L the latent heat of evaporation, and c_{pg} and c_{pF} the gas and fuel specific heats.

Spray Combustion

The relations given above provide some guidance when assessing the atomization and combustion performance of a given system. In reality, however, the actual fluid mechanics, heat transfer and combustion are quite complex. The flow is turbulent, and droplet interactions are usually very important. Figure 9 schematically illustrates the structure of a spay flame. In the interior of the spray, there is usually insufficient oxygen for combustion to occur. As a result, the burning mostly takes place in the periphery of the spray. In the regions where droplet density is high, groups of droplets may burn together, rather than individuals, with diffusion flames surrounding the groups.

In general, most spray flames are more diffusional that premixed in character. As a consequence, combustion takes place in that part of the spray closest to the stoichiometric contour, resulting in peak temperatures close to the stoichiometric adiabatic flame temperature. Because of the flame structure, the droplet receive a fair amount of preheating prior to reaching the burning zone.

Environmental Issues

The general structural characteristics of spray flames, tend to encourage the formation of NO and soot. The former because of high local temperature in the flame zone, and the later because of fuel preheating prior to combustion which tends to encourage carbon formation. Thus efforts to reduce both NOx and soot emissions focus on improving atomization and thus premixing of fuel and oxidizer prior to combustion. Of course other pollutants including CO, unburned hydrocarbons, hazardous air pollutants and metals can be emitted.

Biomass pyrolysis oils are likely to challenge current technology. Because of high viscosity they will be difficult to atomize. Their high molecular weight and charing tendencies will make them susceptable to sooting and to emitting heavier organics. Some fuels apparently contain metals, which may be emitted in sufficient quantities to be of concern.

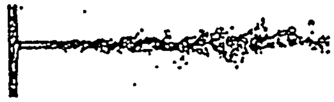
References

1. Lefebvre, A. H., Atomization and Sprays, Hemisphere Publishing Company (1989)

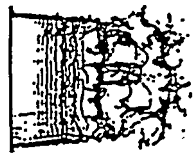
2. Chigier, N. A., "The Atomization and Burning of Liquid Fuel Sprays," Prog. Energy Combust. Sci, Vol. 2, 97-114 (1976)

Atomization

- **Jets**



- **Sheets**



- **Droplets**

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Figure 1

Jet Breakup Regimes

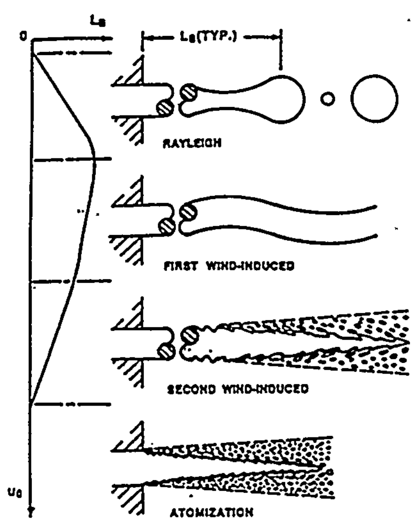

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Figure 2

Jet Breakup Regime Boundaries

- **Reitz and Bracco, 1986**

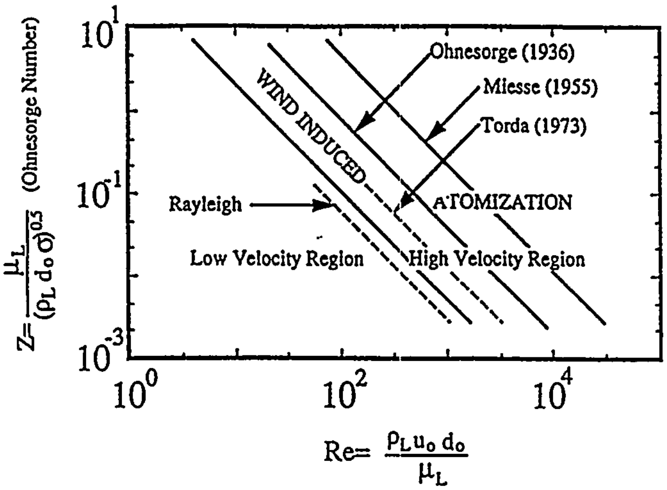

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Figure 3

Types of Atomizer Systems

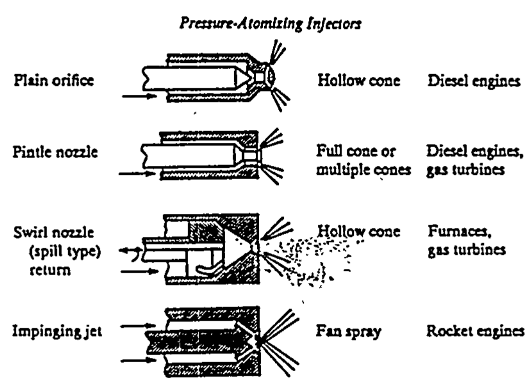

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Figure 4

Types of Atomizer Systems

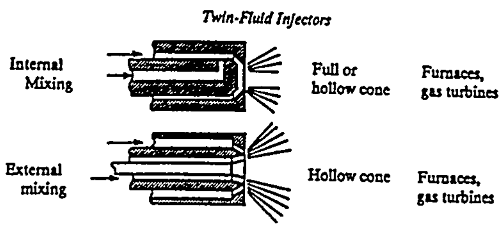

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Figure 5

Types of Atomizer Systems

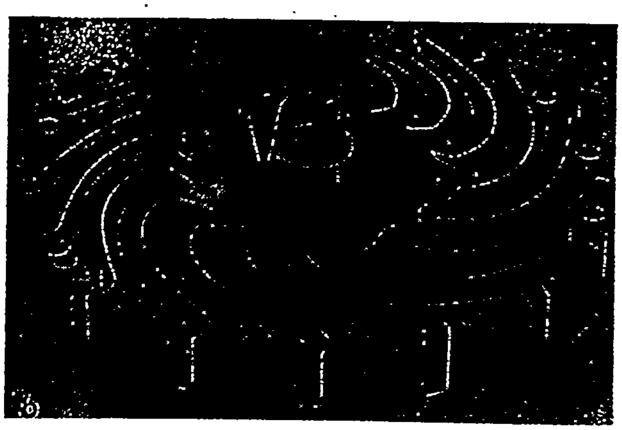

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Figure 6

Atomizer Performance: Size Distribution Functions

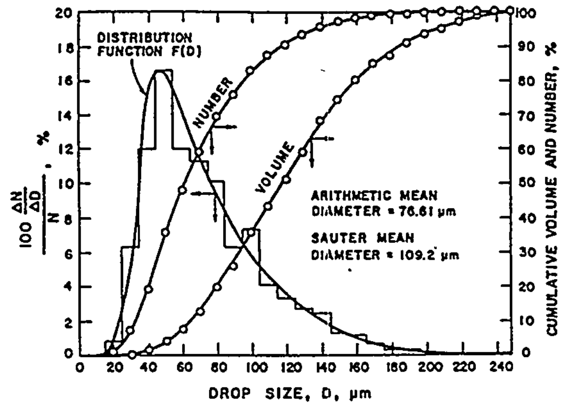

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Figure 7

Atomizer Performance

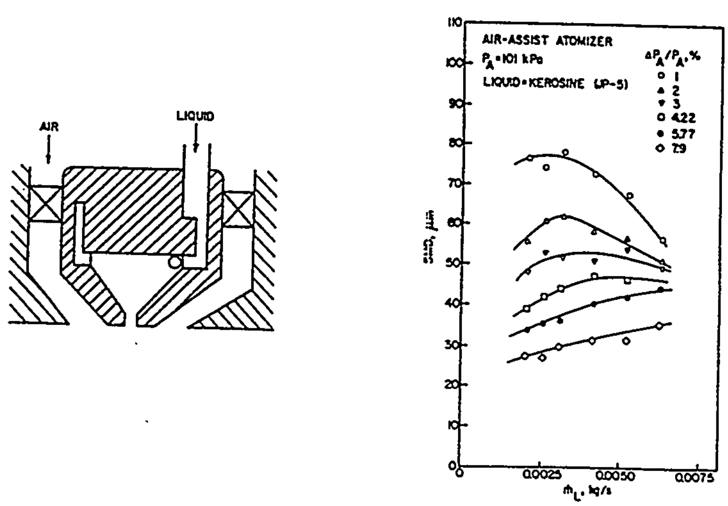

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Figure 8

Spray Flame Structure

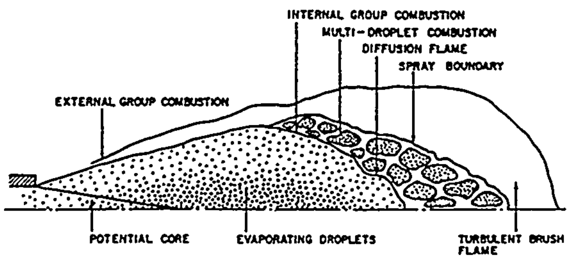

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Figure 9

Formation of Nitrogen Oxides in Combustion Processes

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Oxides of nitrogen may be formed during combustion processes in air by a "thermal" mechanism, by a "prompt" mechanism, or directly from nitrogen containing impurities in the fuel. Thermal NO_x formation refers to NO_x formed from nitrogen and oxygen in air by the extended Zeldovich mechanism. Nitric oxide formation with hydrocarbon fuels may exceed rates of formation attributable to the thermal mechanism because of reactions between CH_i species derived from the fuel and N_2. Finally, nitrogen which is chemically bound in the fuel or a fuel impurity can be rapidly converted to NO_x during the combustion process by direct oxidation. This review will summarize these mechanisms of NO_x formation, characterize the relative importance of the formation processes, and suggest means for ameliorating the formation of NO_x. The importance of NO_x formation and control associated with the combustion of biomass pyrolysis oil products will be emphasized.

References

1. J.A. Miller and C.T. Bowman, "Mechanism and Modeling of Nitrogen Chemistry in Combustion," *Prog. Energy Combust. Sci.*, 15, pp. 287-338, 1989.

2. J. C. Jones, "The Behavior of Nitrogen in Combustion Processes," *Combustion Science: Principles and Practice*, Millennium Books, Newtown, NSW, Australia, 1993.

3. C. T. Bowman, "Chemistry of Gaseous Pollutant Formation and Destruction," in W. Bartok and A.F. Sarofim, *Fossil Fuel Combustion: A Source Book*, Wiley, New York, 1991.

4. C.T. Bowman, "Control of Combustion Generated Nitrogen Oxide Emissions: Technology Driven by Regulation," Twenty Fourth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, pp. 859-878, 1992.

Formation of Nitrogen Oxides in Combustion Processes

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SpecialistsWorkshop on
Biomass Pyrolysis Oil Combustion
September 26-28, 1994

Outline

Introduction

Nitric Oxide Formation Processes
- Thermal NO_x Formation
- Prompt NO_x Formation
- Fuel NO_x Formation

Nitric Oxide Reduction
- Combustion Modification
- Thermal $DeNO_x$
- $RAPRENO_x$

Energetic Material Combustion Studies

Conclusions

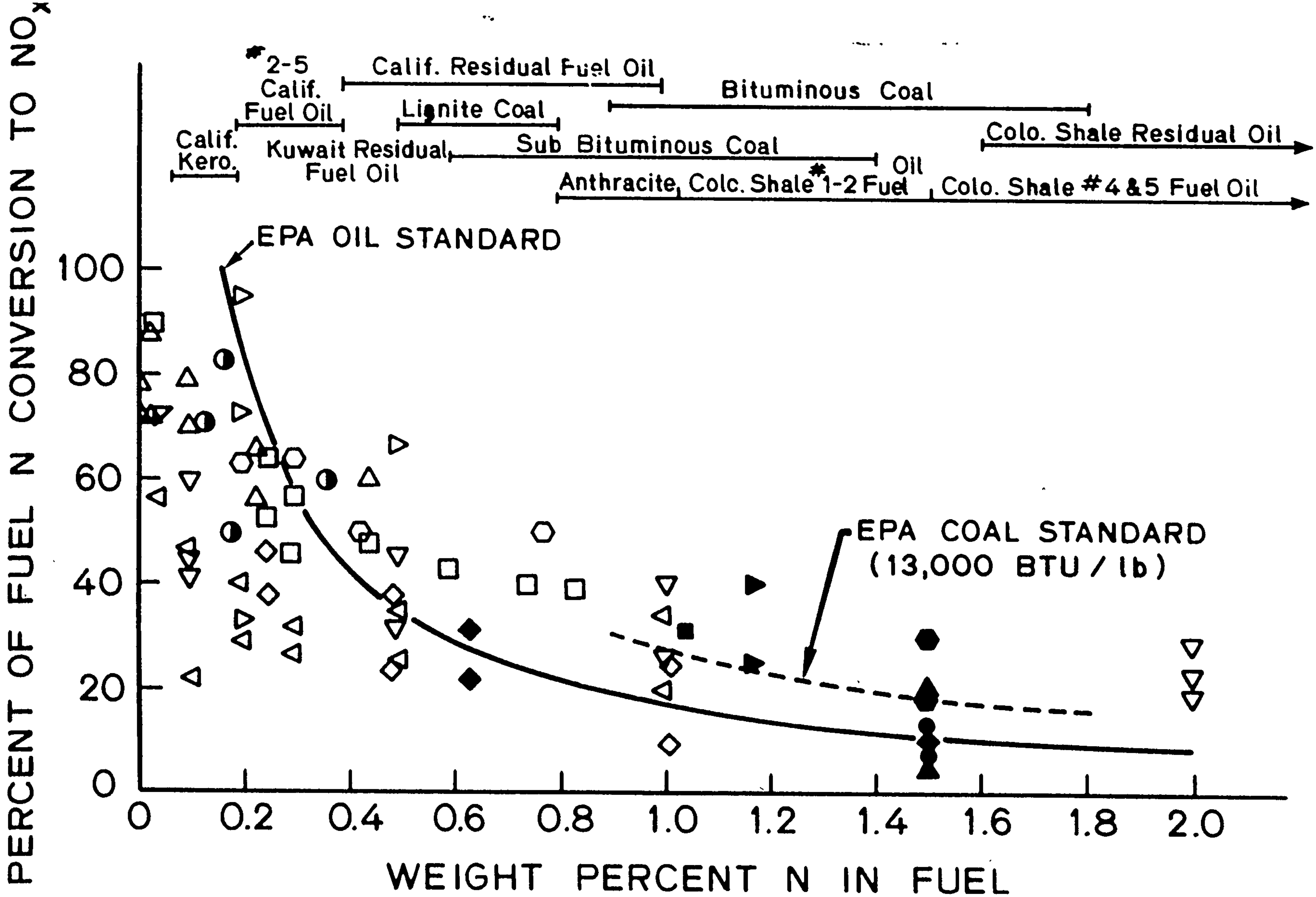


FIGURE 9. Fractional conversion of fuel-nitrogen in fossil fuel combustion in practical devices.[59] Open symbols—oil; solid symbols—coal; semisolid symbols—laminar premixed flames.[32]

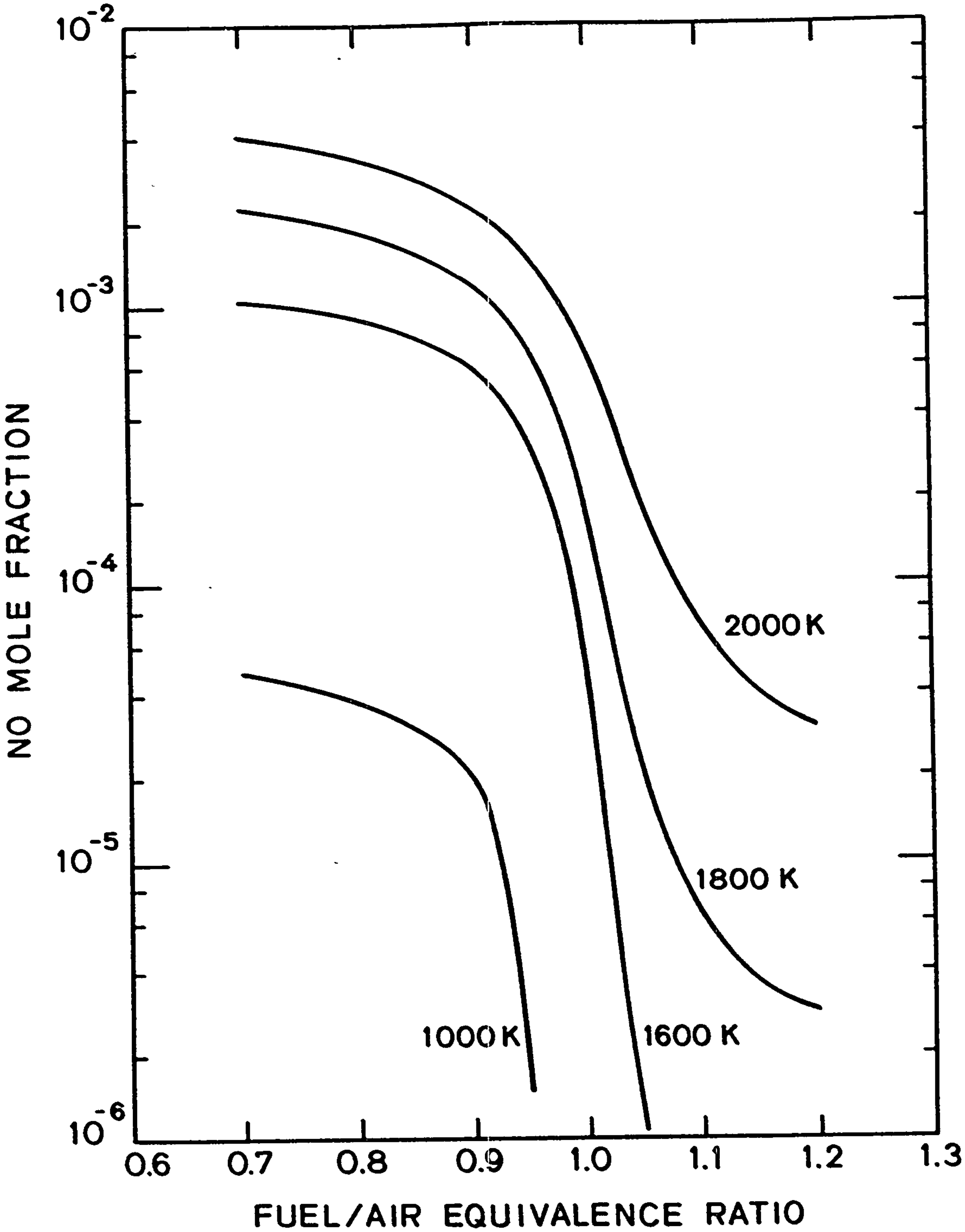
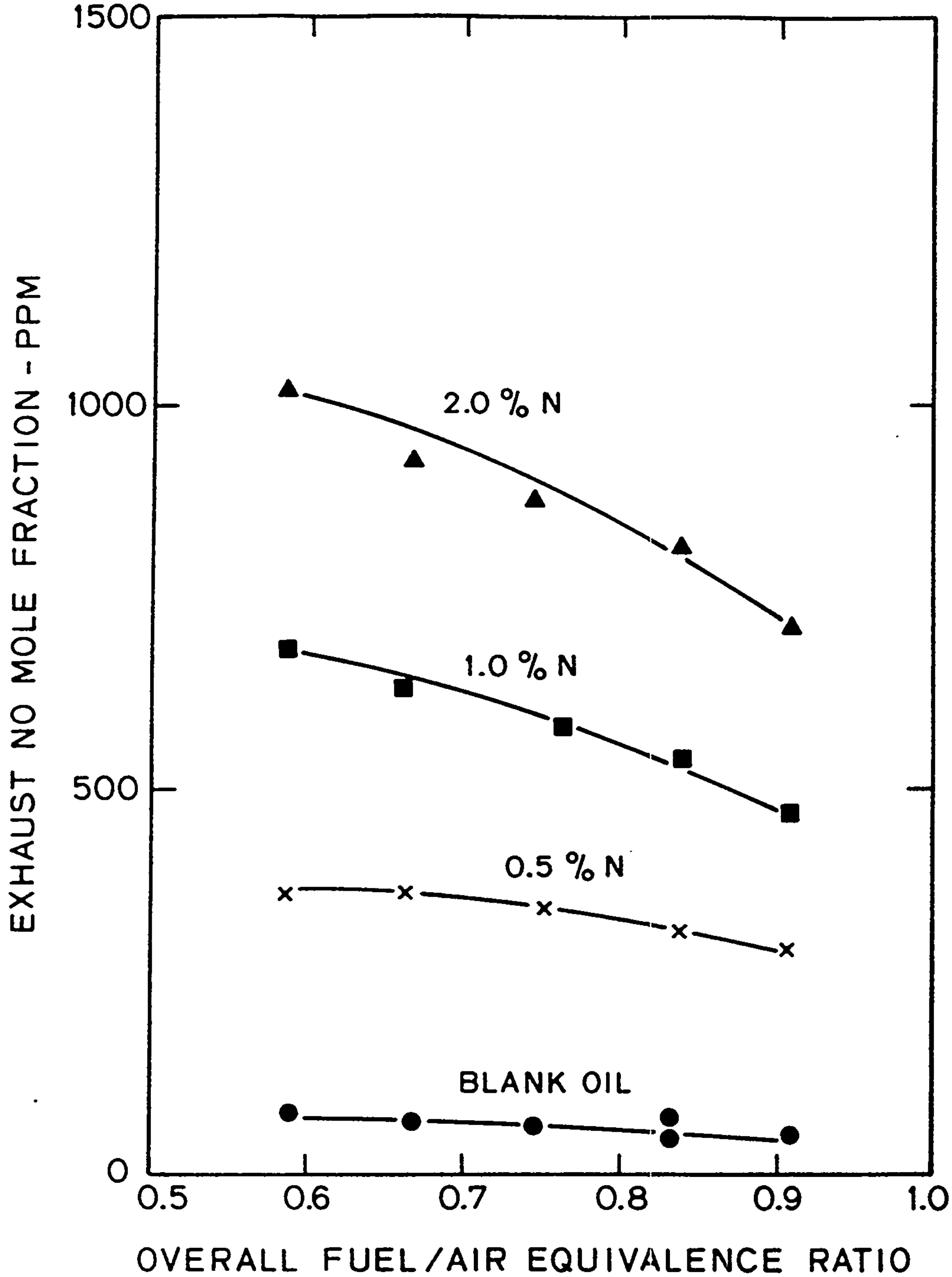


FIGURE 5. Equilibrium NO mole fractions for premixed methane-air combustion pressure of 1 atm.

TABLE 9. The Importance of Prompt NO in NO_x Emissions from Practical Combustion Devices[a]

Device/Fuel	Estimated Percent NO_x Emission due to Prompt NO Mechanism
Utility boiler/natural gas	17
Gas turbine/natural gas	30
SI engine/gasoline	10
CI engine/diesel fuel	5
Utility boiler/coal (N = 1%)	< 5

[a] From Hayhurst and Vince.[20]



Measured exhaust NO mole fractions (dry basis, corrected to stoichiomet-
a oil-fired furnace with various amounts of pyridine (C_5H_5N) added to the

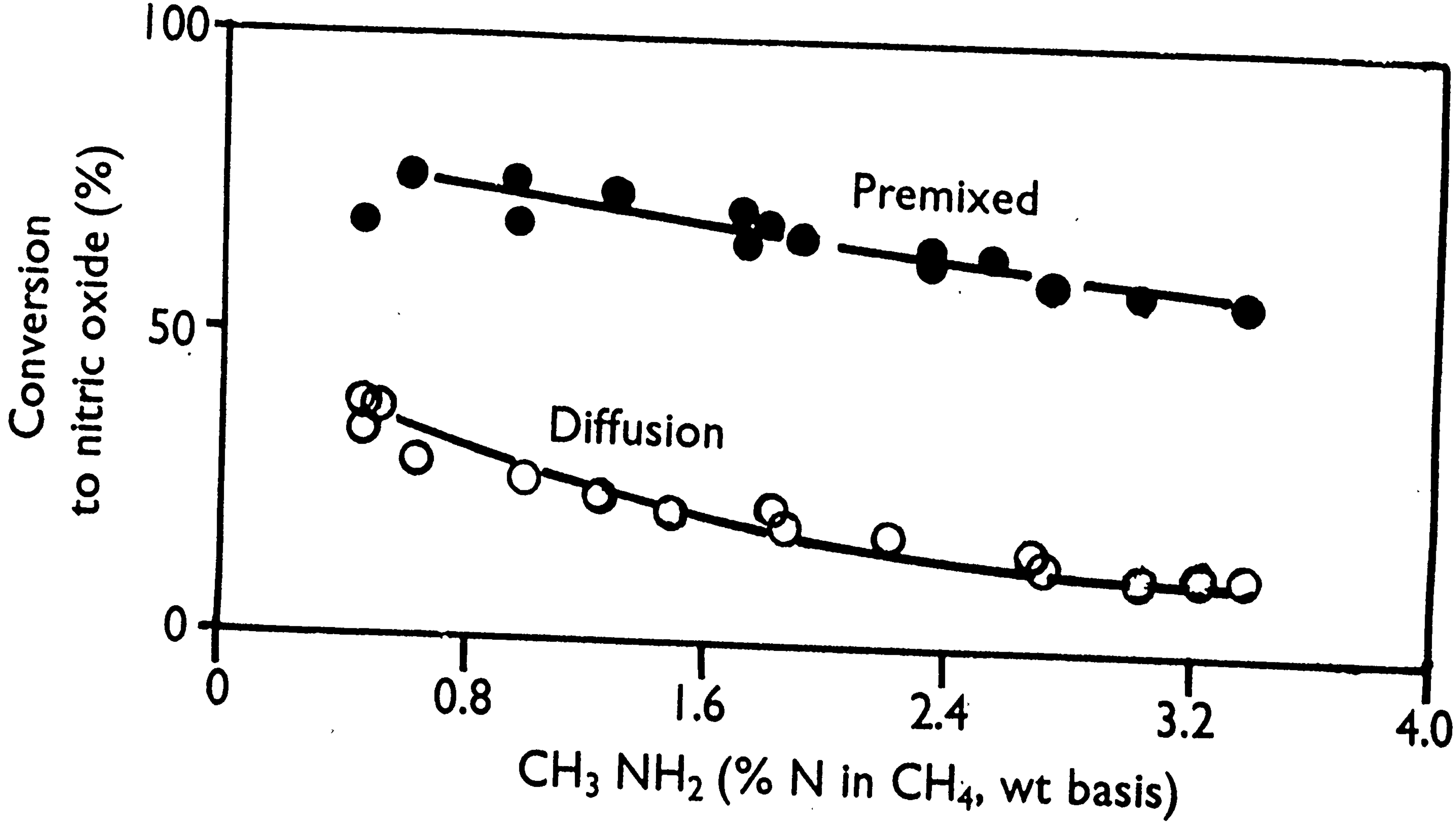


Figure 9.1 Conversion of methylamine to NO_x in lean methane–air flames (Fine et al. [1]) *(Reproduced with the permission of Butterworth–Heinemann.)*

NO_x Formation Mechanisms

Thermal:

$$N_2 + O \rightleftarrows NO + N$$
$$O_2 + N \rightleftarrows NO + O$$
$$N + OH \rightleftarrows NO + H$$

Prompt:

$$CH_i + N_2 \rightleftarrows HCN + NH_{i-1}$$
$$HCN \Rightarrow NCO \Rightarrow NH \Rightarrow NO$$

Fuel:

$$\text{Fuel N} \Rightarrow HCN, NH_2$$

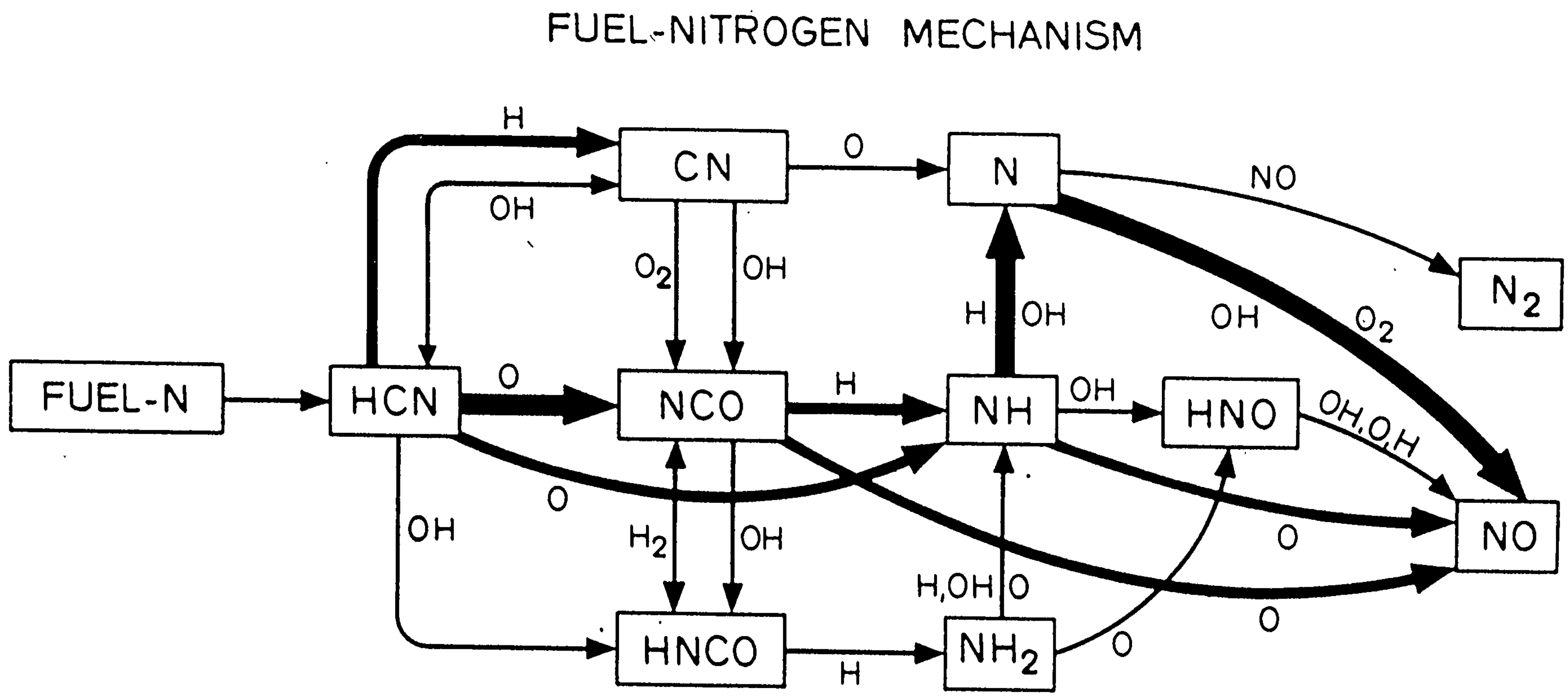


FIGURE 12. Schematic diagram of the principal reaction paths in the fuel nitroge conversion process in flames.

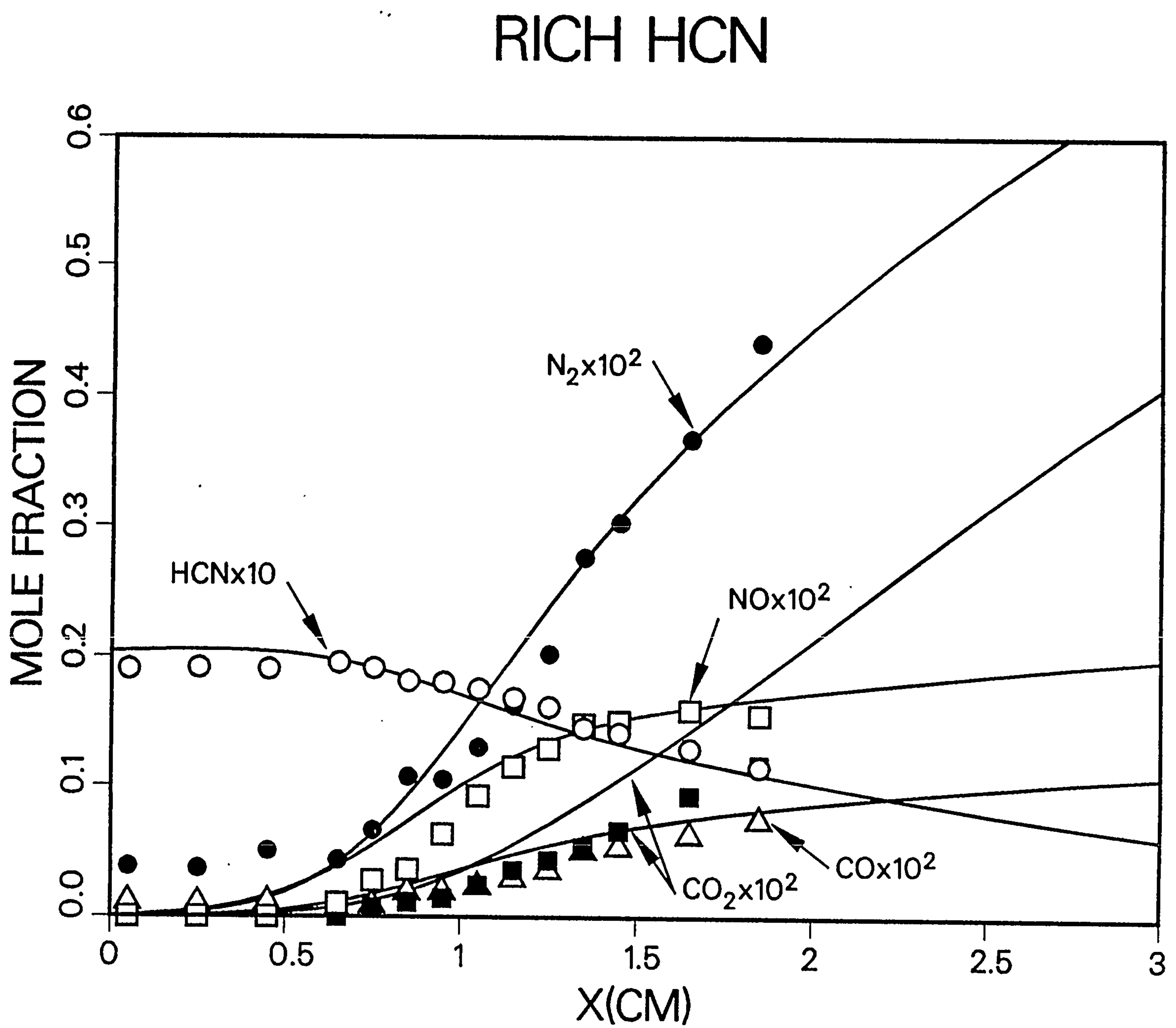


Fig. 16 Comparison of model predictions with the experimental data of Miller et al. [10] for a rich ($\phi = 1.5$) $H_2/O_2/Ar$ flame (p = 25 torr) to which two percent HCN was added.

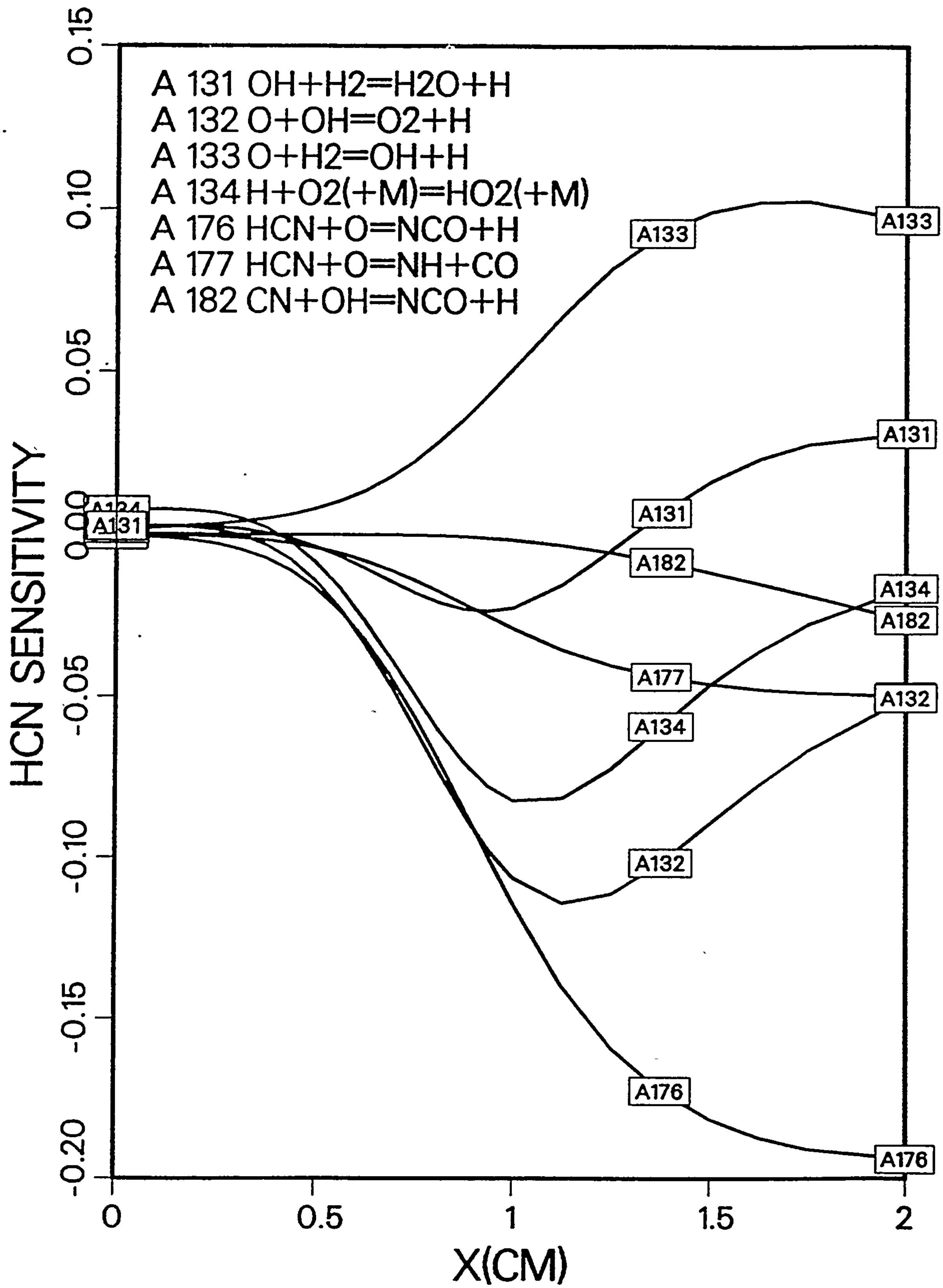
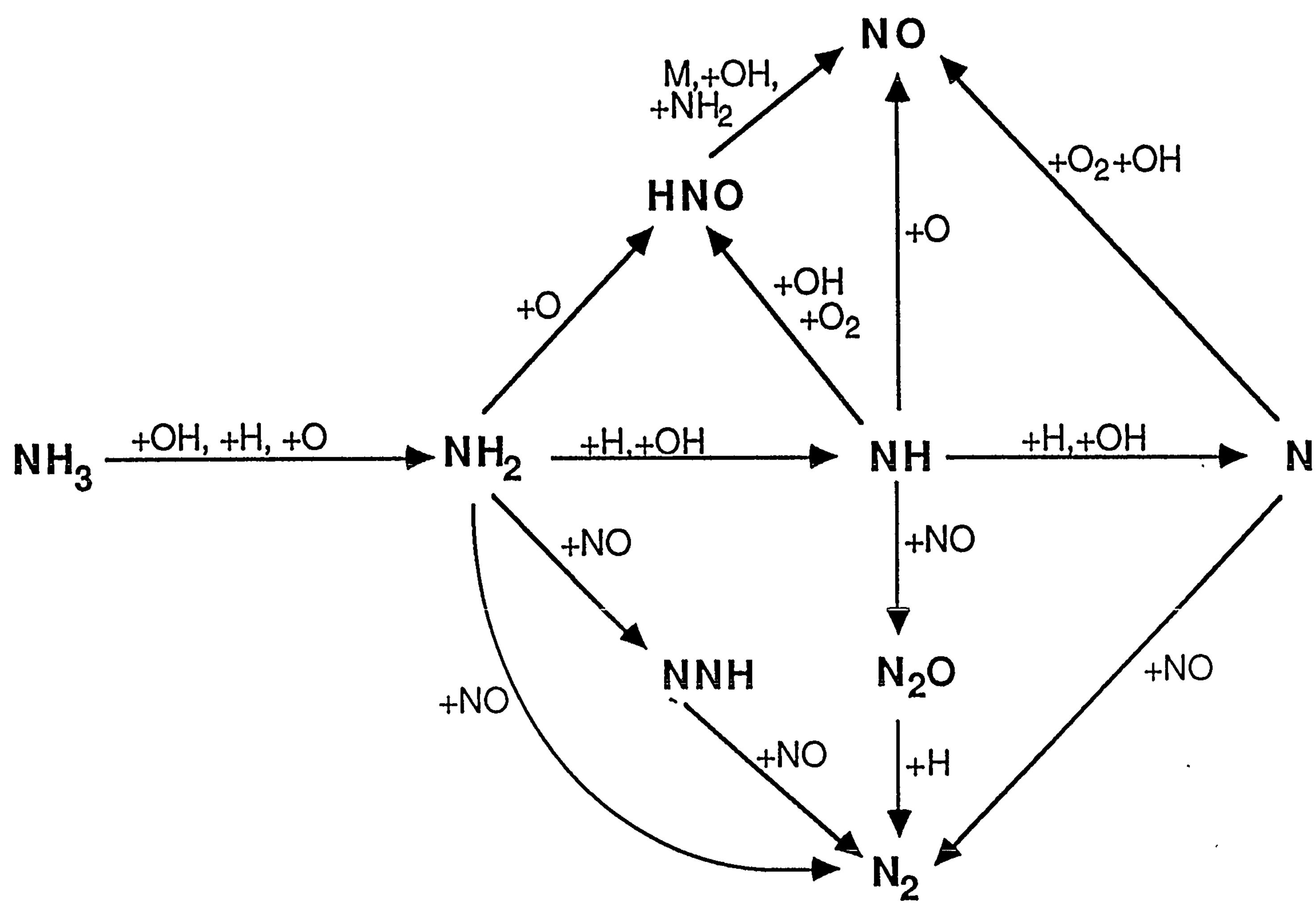


Fig. 18 Sensitivity plot for HCN in the rich flame of Fig. 16.



Reaction path diagram for the oxidation of ammonia in flames.

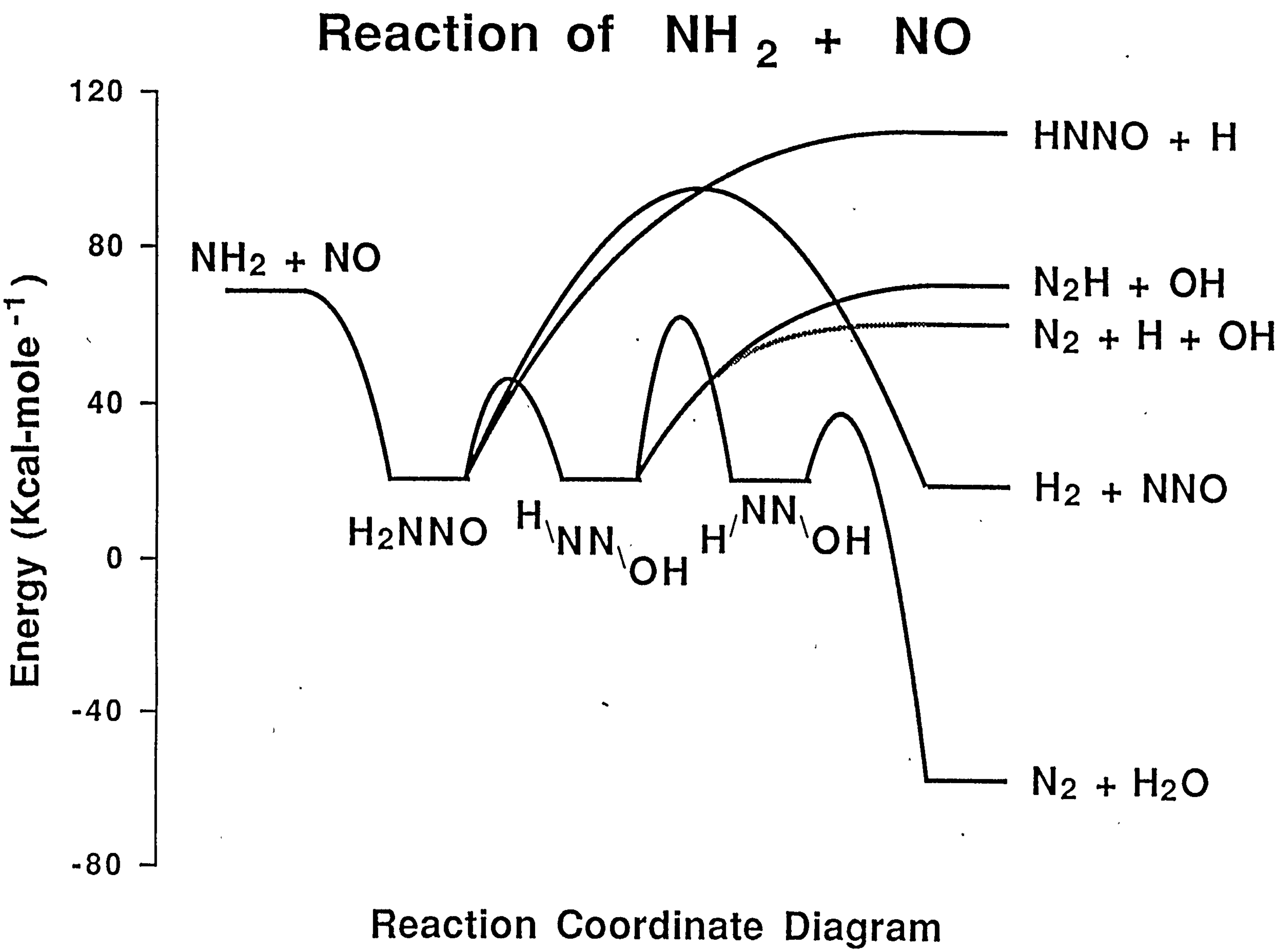


Fig. 59 Reaction coordinate diagram from BAC-MP4 calculations for the reaction $NH_2 + NO \rightarrow$ products.

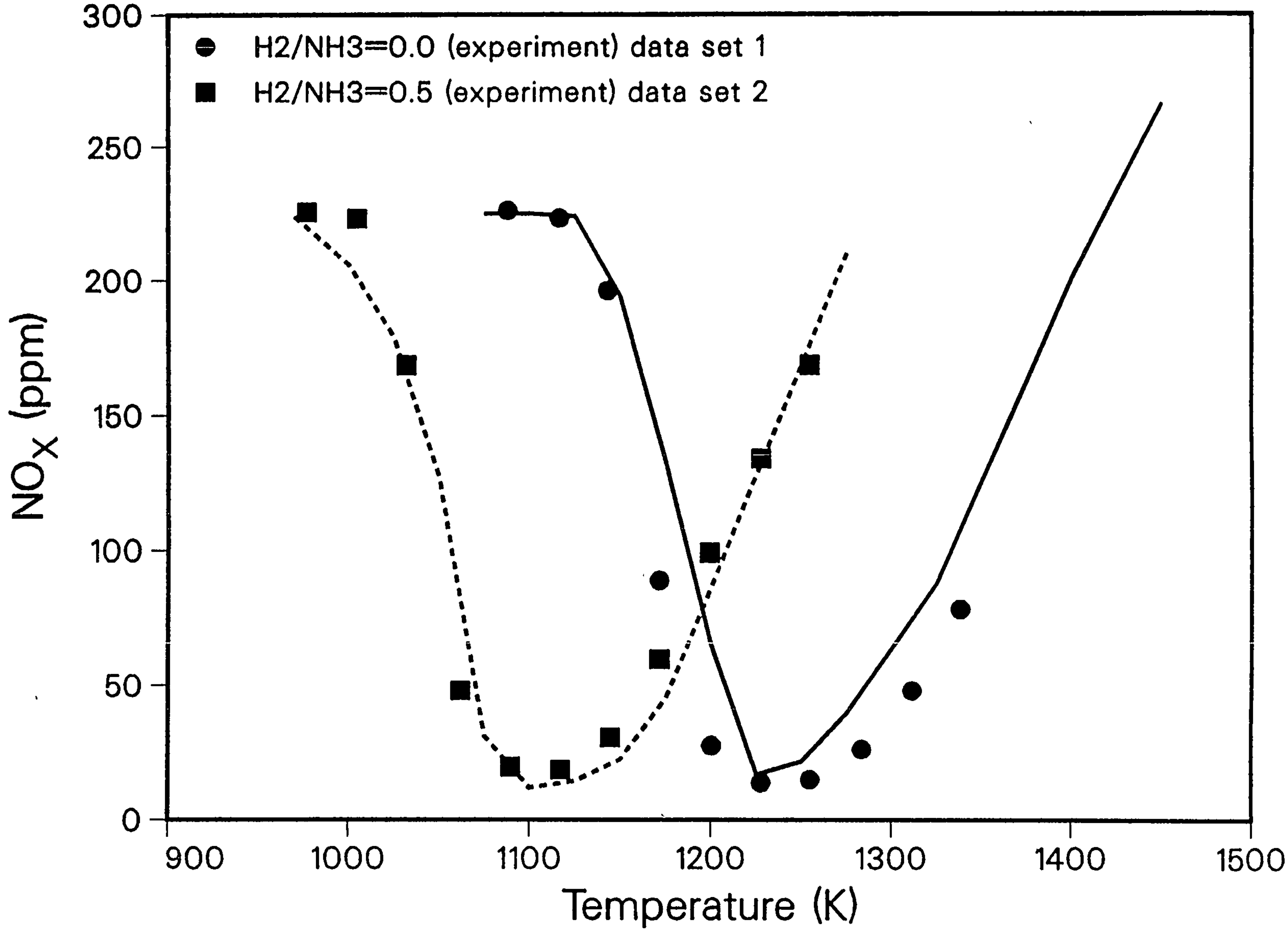


Fig. 49 Comparison of model prediction of the temperature window and the influence of H_2 on the temperature window with experiments for Thermal De-NO_x. Initial conditions for the experiments and calculations are as follows: data set 1: NO = 225 ppm, NH_3 = 450 ppm, O_2 = 1.23%, remainder He, p = 1.1 atm; data set 4: same as data set 1 except 225 ppm H_2 displaces an equal amount of He. Reaction time t = 0.1 sec.

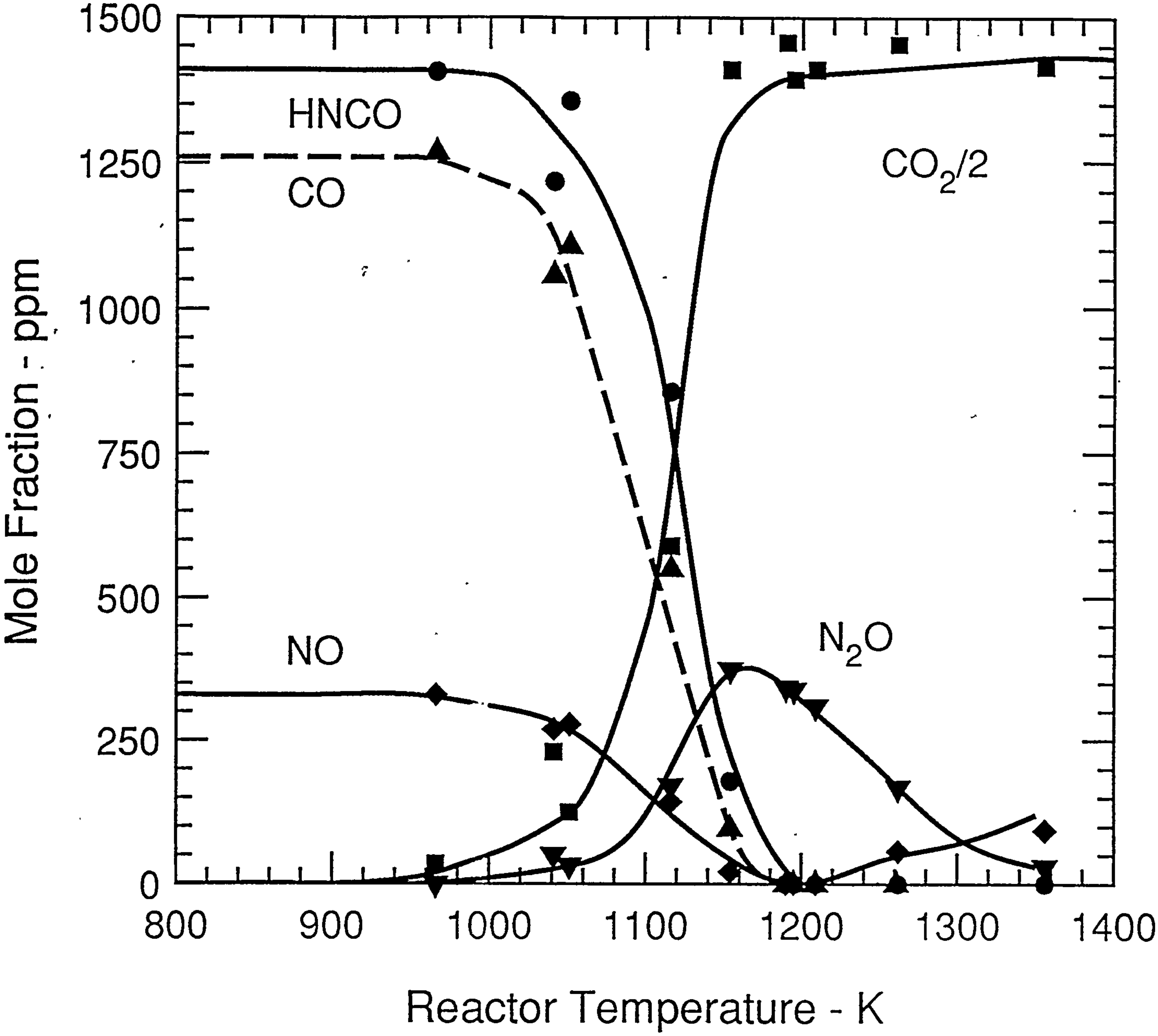


Fig. 63a Measured species concentration at the exit of a quartz flow reactor as a function of reactor temperature for fixed initial mole fractions of NO (330 ppmv), CO (1260 ppmv), O_2 (12.3 percent), H_2O (4.5 percent) and cyanuric acid (470 ppmv, corresponding to 1410 ppmv HNCO at complete conversion). The residence time in the reactor is approximately 0.8 seconds. The data are from Ref. [166].

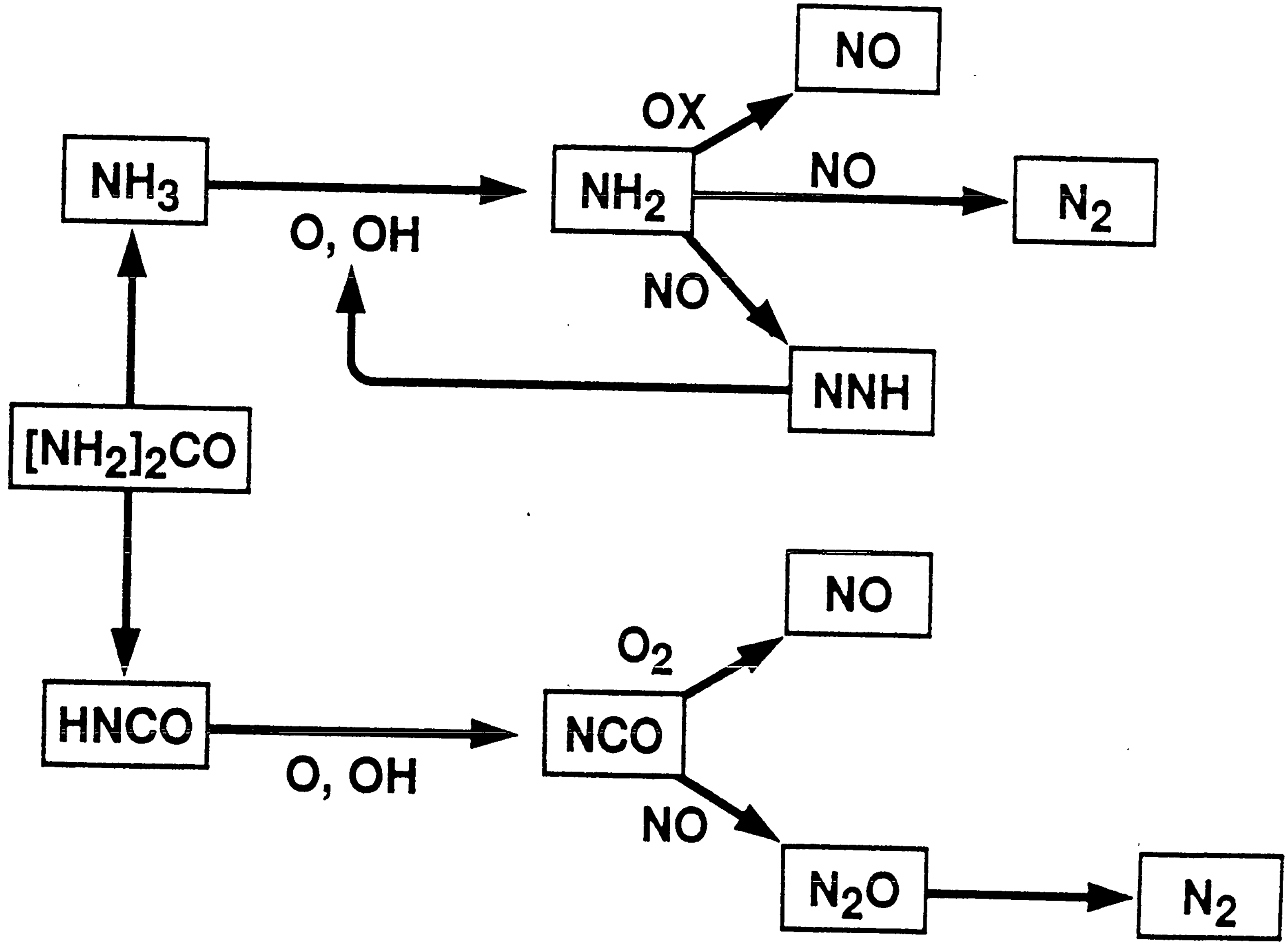


FIG. 5. Reaction path diagram illustrating the major steps in gas-phase NO-removal by reaction with ammonia, isocyanic acid and urea.[33,50,51]

TABLE VI

NO_x Emissions Control Technologies and Potential Emissions Reductions

Fuel	Combustion Source	Control Technology*	Estimated NO_x Emissions: Percent Reduction	Estimated NO_x Emissions: NO_x (ppmv@3% O_2)
atural gas	Boilers	LNB + OFA + FGR	70–80	20–50
		Reburning	50–60	30–50
		SCR	80–90	20–30
	Process heaters	LNB + FGR	70–80	20–50
		Radiant burners	80–90	20–25
	Gas turbines	Water injection	70–80	30–40
		Lean premixed burner	80–90	10–20
		SCR	80–90	10–20
uel Oil	Boilers	LNB + OFA + FGR	70–80	70–100
		SCR**	80–90	30–50
	Stationary Diesels	SNCR	70–90	50–60
ulverized oal	Wall-fired/ tangential-fired boilers	LNB + OFA	60–70	150–250
		Reburning	50–60	100–150
		SNCR**	30–75	100–200
		SCR**	80–90	80–100
	Cyclone-fired boilers	Reburning	50–60	150–200
		SNCR	30–75	200–350
		SCR	80–90	100–150
	Fluid bed combustors	Staging	50–60	100–150
		SNCR	70–80	30–120
		SCR	80–90	30–60
asoline	SI engines	Three-way catalyst	90–95	0.2 g/mi

*LNB = Low-NO_x Burner; OFA = Overfire air, FGR = flue gas recirculation; SCR = Selective Catalytic Reduction; SNCR = Selective Non-Catalytic Reduction.

**in conjunction with LNB + OFA

Conclusions

Mechanisms of NOx formation and removal are reasonably well defined for conventional fuels and nitrogen impurities.

Rate data for elementary reactions are under continuing development.

Possible interference from minor constituents of Biomass Pyrolysis Oil have been studied less thoroughly.

Single Droplet Combustion of Biomass Pyrolysis Oils

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Single Droplet Combustion of Biomass Pyrolysis Oils

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Introduction

Because of its renewability and availability, one of the more attractive alternatives to conventional energy sources is biomass, which includes wood, agricultural residues, and fast-growing crops. Although many forms of biomass can be burned directly as combustor fuels,[1,2] the pyrolysis and liquefaction of biomass[3–9] lead to solid and liquid fuels of lower moisture content. For certain specialized applications, additionally upgraded fuels can be produced from thermochemical treatment of biomass pyrolysis products.[6,7,10–13]

Our current work concerns the combustion of chars and oils produced from biomass pyrolysis. The combustion of biomass chars is treated elsewhere.[14,15] This paper focuses on the combustion of oils produced from the pyrolysis of wood. Since wood comprises principally lignin, cellulose, and hemicellulose,[16–18] the oxygen-rich nature of these components is reflected in the products

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of pyrolysis at low to moderate temperatures: organic acids, aldehydes, ketones, furans, alcohols, phenols, guiacols, syringols, and complex organic oxygenates.[18-21] High levels of both oxygenated organics and water distinguish biomass oils from petroleum-based liquid fuels. These oxygen-rich constituents influence the physical properties of the fuel as well as their behavior during combustion.

Another characteristic of the biomass oils, relevant to combustion, is their multicomponent nature. Several works[22-27] address the issues of heat and mass transport relevant to the evaporation and combustion of multicomponent fuels. In many cases, droplet swelling and/or fragmentation occurs as a consequence of the presence of components with a wide range of volatilities.[27,28] The formation of carbonaceous residues, including cenospheres, has also been observed.[28,29]

In our present study, we investigate the overall combustion behavior of oils produced from the rapid, moderate-temperature pyrolysis of two biomass feedstocks—a hard wood, oak; and a soft wood, Southern pine. In order to accentuate the features of combustion peculiar to biomass oils and to facilitate comparison of biomass oils with more conventional fuels, we choose single droplet combustion in a laminar flow environment, where droplets are uniformly sized, moving in a well-characterized flow field, and widely spaced so as not to incur interactions with other droplets. In the present paper, we report the time-resolved combustion history of oak and pine pyrolysis oils—presenting *in-situ* images of the oils and the products of their partial reaction at various stages throughout their combustion lifetime. We interpret the results in light of the characteristic features of these biomass-derived fuels and make comparisons to liquid hydrocarbon fuels, as appropriate.

Experimental Materials, Equipment, and Procedures

Combustion experiments are conducted on a sample of No. 2 fuel oil and on two biomass pyrolysis oils. The No. 2 fuel oil, supplied by Union Oil of California, has density, 0.86 g/cm^3; viscosity, 2.2 cP (at 40 °C); and a boiling point range of 182–351 °C.

Table 1. Characteristics of the Biomass Oils

	Oak Oil 154	Pine Oil 150
vapor cracker temperature (°C)	450	510
proximate analysis		
ash (wt %)	0.05	0.05
water (wt %)	16.1	18.5
volatiles (diff., wt %)	69.75	65.95
fixed carbon (wt %)	14.1	15.5
elemental analysis (water-free basis)		
carbon (wt %)	55.6	56.3
hydrogen (wt %)	5.0	6.5
oxygen (diff., wt %)	39.2	36.9
nitrogen (wt %)	0.1	0.3
sulfur (wt %)	<0.05	<0.05
calcium (ppm)	80	60
potassium (ppm)	40	<10
sodium (ppm)	10	10
higher heating value (MJ/kg)	22.5	23.0
pH	2.8	2.9
density (g/mL)	1.23	1.21
viscosity (cP)		
at 21 °C	666	175
at 30 °C	322	96
at 40 °C	141	53
at 50 °C	80	30

The biomass oils are produced by the National Renewable Energy Laboratory (Golden, CO) from the pyrolysis of oak or pine particles in a vortex reactor operating at 625 °C and coupled to a vapor cracker.[3] The oak and pine oils of this study result from vapor cracker temperatures of 450 and 510 °C, respectively. Because some char particles are entrained into the vapor cracker, the biomass oils are filtered prior to the combustion experiments.

The characteristics of the oak and pine oils are listed in Table 1. Relative to petroleum-based liquid fuels, the biomass pyrolysis oils contain large amounts of water and organic oxygenates and are quite acidic. The components of the biomass oils also span a wide range of volatilities. The viscosities of the two biomass oils differ substantially, as do their physical states. As Figure 1 portrays, the oak oil is a continuum (the dark spherical inclusion is an air bubble), whereas the pine oil appears to be a suspension with solids that are not fully solubilized at room temperature. Neither of the oils displays evidence of an emulsion character, which would be manifested as a dispersion of multiple miniature spherical droplets within a continuous phase.[30]

The pyrolysis oil combustion experiments are conducted in Sandia's Biomass Fuels Combustion System (BFCS), which consists of a droplet generator, a laminar flow reactor, and a video imaging system. Illustrated in Figure 2, the droplet generator is an adaptation of the design by Green *et al.*,[31] which features droplet production by the application of aerodynamic principles. Biomass oil is pumped slowly by syringe pump through the inner capillary tube and is disengaged as a droplet when the surface tension holding the liquid at the capillary tip is overcome by the drag force of the coaxial gas flow. A cooling jacket surrounding the coaxial gas prevents in-line boiling of biomass oils with highly volatile components. The aerodynamic droplet generator produces uniformly sized droplets of 300–700 μm, spaced greater than 60 diameters apart to ensure that the droplets burn independently of one another.[27,32]

The biomass oil droplets are released downwardly into the centerline of the BFCS laminar flow reactor, operating at a total gas flow of 49 L(STD)/min. A laminar flow burner at the top of the reactor provides the high-temperature gas environment for the combustion experiments. A mixture of

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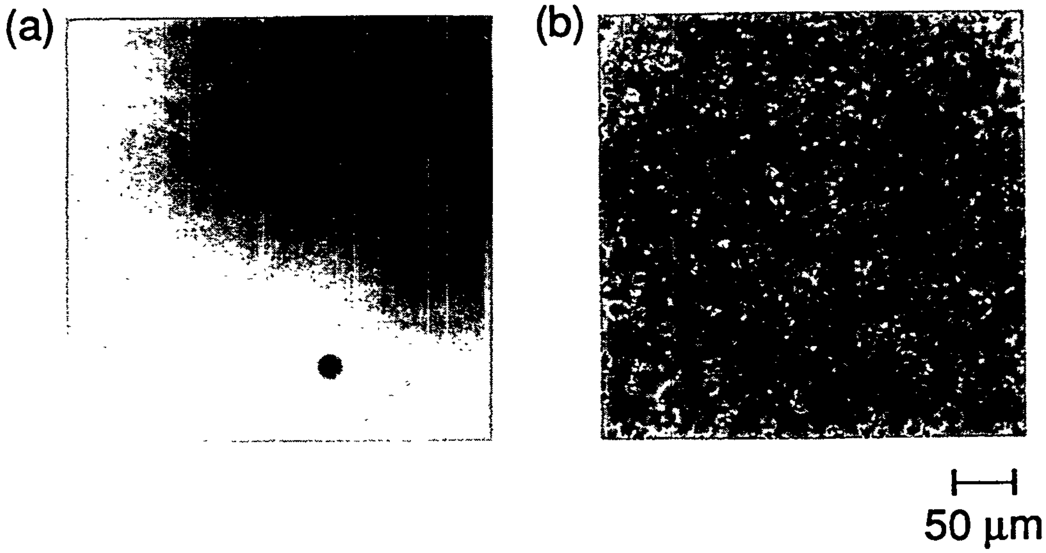

Figure 1. Photographs of filtered biomass pyrolysis oils. Magnification, 150×. (a) Oak oil; (b) pine oil. The dark sphere in (a) is an air bubble.

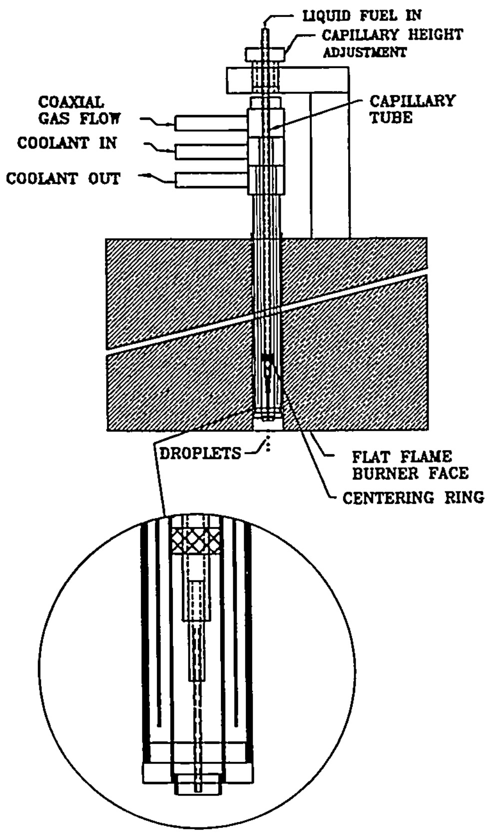

Figure 2. BFCS aerodynamic droplet generator.

hydrogen and methane is supplied through each of the more than 600 fuel tubes. Oxygen/nitrogen mixtures are fed through the honeycomb surrounding the fuel tubes—forming small diffusion flames at each fuel tube end. The stoichiometry of the reactor's $H_2/CH_4/O_2/N_2$ flame is tailored to produce 1600 K postflame gases with oxygen concentrations of 14–33 mol %. The quartz walls of the BFCS reactor provide optical access for imaging of the burning droplets.

In-situ imaging of burning biomass droplets is accomplished with a Panasonic WV-CL700 super-VHS stationary charge-coupled device camera, a Panasonic AG-7350 super-VHS recorder, and a Sony PVM 1342Q super-VHS monitor. Back lighting is provided by a strobe, which is laser-triggered to flash when a droplet passes through the focal point of the system. Adjustment of the vertical position of the reactor, relative to the optical system, permits imaging at different heights along the reactor chimney so that droplet sizes, morphologies, and velocities can be monitored as functions of residence time.

Droplet velocities are measured along the length of the reactor so that droplet residence times can be determined as a function of distance. To make the measurement, the laser trigger system is programmed to signal the back-lighting strobe with two pulses, separated by 500 μs. The video camera records the two positions of the droplet, and the droplet velocity is calculated by dividing the distance of separation by the time of pulse spacing. The instantaneous values of the reciprocal of velocity are then integrated over the distance along the reactor in order to calculate droplet residence times.

In selected biomass oil combustion experiments, solid residues are collected manually from the exhaust stream of the BFCS reactor for subsequent analysis. Particle morphology and surface composition are determined by secondary electron imaging on a JEOL Model 840 scanning electron microscope (SEM), operating at 15 kV, and by energy-dispersive X-ray spectrometry (EDS) with a Tracor Northern 5502 spectrometer.

Combustion experiments on biomass oil solid residues from the BFCS reactor are conducted in Sandia's Captive Particle Imaging (CPI) system, described in detail by Hurt and Davis.[33] In this reactor, particles are placed on a low-density support and inserted into the flow reactor through an open test section in the quartz reactor wall. The support is surrounded by a small conical cooling coil that maintains the particle at 200–300 °C, while it is brought into the focal volume of a modified long-focal-length microscope. The cooling coil is then retracted, the particle is rapidly heated by the surrounding gases, and its ignition, combustion, and burnout behavior are imaged with reflected visible light.

Results and Discussion

BFCS Combustion Experiments with No. 2 Fuel Oil. When introduced into the BFCS reactor at 24 mol % O_2, 320 μm droplets of No. 2 fuel oil ignite at 7 ms and burn quiescently until full burnout is achieved at 139 ms. Except for the initial millisecond and final two milliseconds (which are accompanied by a blue flame), No. 2 fuel oil droplets burn in a yellow flame indicative

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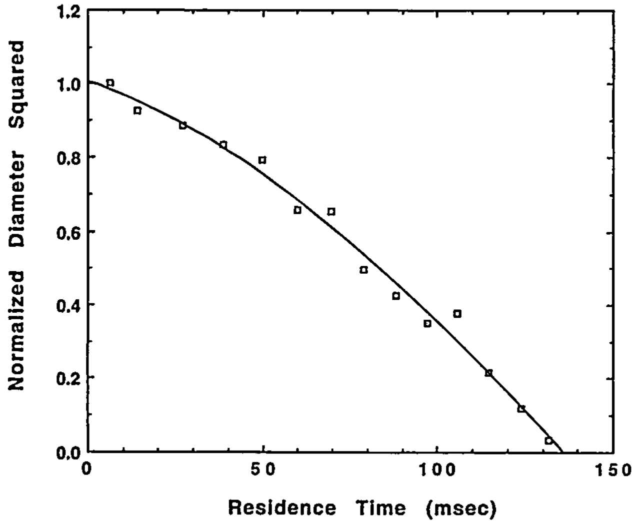

Figure 3. Normalized droplet diameter squared as a function of residence time in the BFCS reactor for No. 2 fuel oil. Instantaneous droplet diameters normalized to the initial droplet diameter of 320 μm. Gas composition, 24 mol % O_2.

of soot. Other than soot, no carbonaceous solids are produced during the combustion of No. 2 fuel oil in the BFCS reactor. The soot-forming and non-coking tendencies of No. 2 fuel oil have been previously noted.[34]

Figure 3 displays the monotonic decrease in droplet size as the No. 2 oil burns in the BFCS reactor. For a single-component fuel burning at steady state, a plot of diameter squared versus time is linear, in accordance with the constant surface regression rate characteristic of heat and mass diffusion control.[25] The slight curvature in the data of Figure 3 is consistent with literature results on the quiescent burning of nonviscous solutions of components with a fairly narrow range of volatilities.[25,28]

BFCS Combustion Experiments with Oak Oil. Biomass oil burns very differently from No. 2 fuel oil. Figure 4 portrays oak oil droplets burning in an atmosphere of 24 mol % O_2 in the BFCS reactor. Evident from the photograph are the different stages of biomass oil droplet combustion. After release from the droplet generator, the droplets ignite at a residence time of approximately 12 ms and burn quiescently in a spherical blue flame approximately two droplet diameters wide. Due to the long exposure time of the photograph (3 min), the burning of thousands of droplets is recorded in Figure 4, and the succession of moving spherical blue flames appears as a continuous blue streak.

After 34 ms, droplet burning is briefly accompanied by the onset of broadband luminosity, which appears as the bright oval-shaped region, about 5 mm in diameter, in Figure 4. Very small luminous fragments are occasionally observed to be released from this luminous region. The broadband luminous burning gives way to a fainter, smaller-diameter blue flame, occasionally punctuated with additional luminous bursts that are much smaller scale than the initial broadband luminous event. Combustion of the biomass oil concludes in a yellow flame, indicative of the presence of soot.

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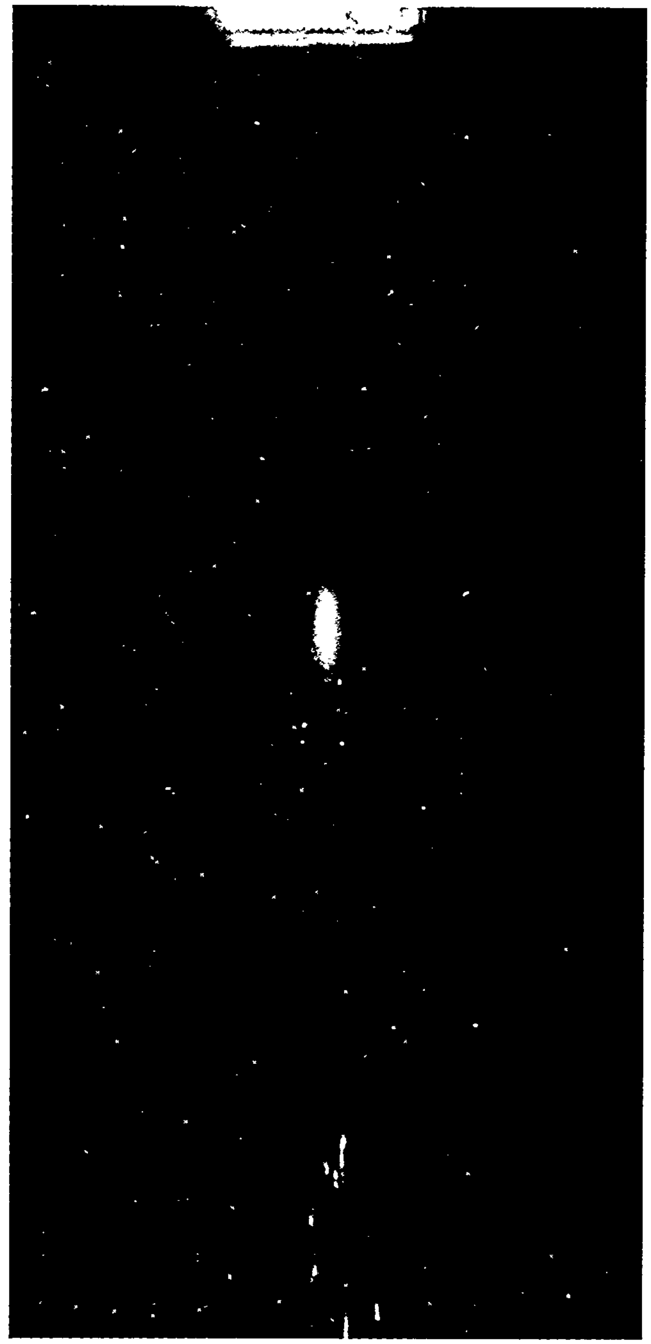

Figure 4. Photograph of oak oil droplets burning in the BFCS reactor at 24 mol % O_2. Blue flame enhanced during photographic development.

Figure 5 presents *in-situ* video images of droplets of oak oil, initially 320 μm in diameter, burning in 24 mol % O_2 for residence times of 21–121 ms, corresponding to the different stages of burning. Under these conditions, full burnout occurs at 149 ms. Because the exposure time is only 1 μs (the duration of a pulse from the laser-triggered strobe), these images of moving droplets are frozen at each selected residence time. The intensity of the strobe, the source of the back-lighting, overwhelms any luminosity from the flame, so no details of the flame are evident from the images in Figure 5.

Figure 5a depicts the quiescent phase of biomass oil droplet combustion, sustained from 12 to 34 ms, during which burning occurs in a blue flame and the spherical shape of the droplet is not perturbed. Similar behavior is observed throughout the combustion lifetime of

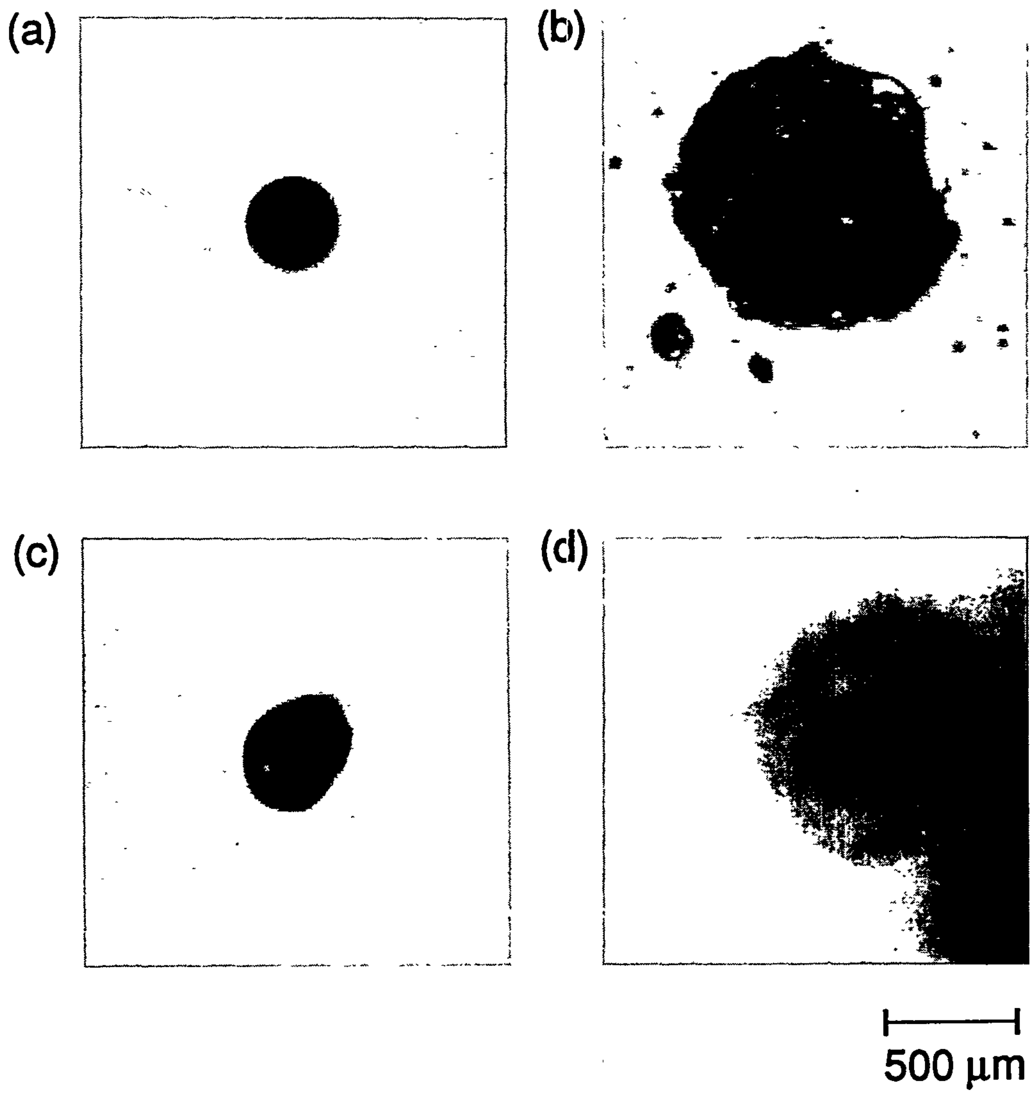

Figure 5. Video images of droplets of oak oil, burning at 24 mol % O_2 in the BFCS reactor. Residence times of (a) 21.4 ms; (b) 34.8 ms; (c) 42.7 ms; (d) 121.2 ms.

droplets of pure methanol or acetone in the BFCS reactor. The quiescent combustion stage of the oak oil terminates, however, at 34 ms, the residence time corresponding to the beginning of the broadband luminous region in Figure 4. Here the droplet images change abruptly, as demonstrated in Figure 5b. As Figure 5b reveals, combustion at this stage is characterized by sudden buildup of vapor within the droplet, leading to expansion and distortion of the droplet. Rupture of the droplet surface is accompanied by the release of fuel vapor and small droplet fragments—most with diameters of tens of microns or less. Successive images of the same droplet, not shown here, reveal that droplet expansion occurs within 500 μs. As noted by Yap *et al.*[35] for the combustion of hexane/hexadecane mixtures, the broadband luminosity observed during the microexplosion most probably results from radiating soot particles produced by gas-phase pyrolysis of fuel vapor, present at high concentration in the vicinity of the droplets at the time of the microexplosion.

After the release of vapor during the microexplosion, oak oil droplets coalesce, due to surface tension, as depicted in Figure 5c. Burning at this stage occurs again in a blue flame, fainter than the first. The nonspherical shape and small yet identifiable regions of transparency in the droplet of Figure 5c indicate that vapor is still trapped inside droplets at this stage, although droplet swelling is not as pronounced at this longer residence time.

The final stage of burning of oak oil is depicted by the droplet in Figure 5d, taken at a residence time of 121 ms. This image reveals that droplets at this stage are indeed surrounded by a soot cloud, which accounts for the observed yellow flame. It is also interesting to note that even though this residence time corresponds to the last 30 ms of burning, droplets are still of an appreciable size.

In the evaporation and combustion of multicomponent liquid fuel droplets, there are two extremes of behavior.[22–24,36] In the first, corresponding to low values of the liquid-phase Peclet number *Pe* or Lewis number *Le*, mass transfer within the liquid phase is rapid, and surface regression due to evaporation is balanced by the migration of volatilizing components to the droplet

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surface. This "batch distillation" mechanism is favored in situations of rapid internal circulation, which may be induced by large relative velocities between droplet and gas. The other extreme, favored by highly viscous liquids with minimal internal circulation, corresponds to high *Pe* and *Le* and to rate control by liquid-phase mass transfer. In this case, pockets of vapor build up within the droplet as a result of the nucleation of volatilizing components that are deterred from reaching the droplet surface. Swelling of the vapor-filled droplet occurs until surface tension forces, holding the droplet together, can no longer balance the pressure differential across the liquid surface. At that point, the droplet surface ruptures, resulting in a microexplosion.

The combustion of biomass oils adheres more closely to the latter of the above extreme cases for three reasons: the biomass oils are viscous; internal circulation within the droplets is low, due to the low droplet Reynolds number *Re* of our system ($Re \approx 2$); and the biomass oils comprise components of a wide range of volatilities. The physical properties of biomass oil also change during a droplet's combustion lifetime, as volatile species evaporate and remaining species undergo thermally induced chemical transformations that could lead to higher viscosity. Quiescent burning of the biomass oil occurs until the temperature at some position within the droplet reaches the local homogeneous nucleation temperature.[37] For oak oil, that point is reached at a residence time of 34.8 msec, when the microexplosion occurs. Our observation of the time of droplet expansion of <500 μsec is consistent with the observations of Lasheras *et al.*[38] that homogeneous nucleation occurs in a time scale on the order of 100 μsec.

The sequence of quiescent burning followed by microexplosion has been observed for a variety of other multicomponent fuels: mixtures of alkanes;[35] alkane/alcohol mixtures;[37,39] alcohol/ether solutions;[39] residual oils;[40] heavy fuel oil;[41] ethanol/No. 2 fuel oil mixtures;[42] alkane/water emulsions;[43] and an alkane with dissolved pyrolysis products.[44] As Lasheras *et al.*[42,45] observe, the manner of the microexplosion depends on whether the multicomponent fuel is a solution or an emulsion. Differences in the two cases arise as consequences of differences in fluid "structure," the conditions for internal boiling, and the nature and growth of the bubbles formed during nucleation.[42,45] A major difference between fuel solutions and emulsions concerns swelling. In solutions, droplet diameters may increase by a factor of 3[37] prior to the microexplosion. In the case of emulsions, however, where droplets of 1–5 μm are dispersed throughout a continuous phase, no swelling of the overall emulsion droplets occurs prior to disruptive fragmentation.[45]

Figure 6 portrays four oak oil droplets at the time of microexplosion. Despite the high water content (16.1%) of the oak oil, it appears to behave more like a multicomponent solution than an emulsion since the oak oil droplets swell by up to a factor of 3 in diameter prior to rupturing. This behavior is consistent with the one-phase nature evident in Figure 1.

Compared to the *in-situ* images of swollen droplets of other multicomponent fuels during combustion,[35,37,42,45] those of the biomass oils appear to be unique. The oak oil droplets in Figure 6 exhibit a departure from sphericity and an irregular distribution of outer surface thickness during the microexplosion. Numerous bubbles, bordered by liquid membranes, appear to be present within the swollen biomass oil droplets. One possible explanation of the unique appearance of the swollen biomass oil droplets is the high concentration of oxygen-containing organic species, which make this fuel more prone to polymerization reactions.[20,46] These biomass oils are known to polymerize over a period of days at a temperature of 37 °C and hours at 90 °C.[47] At the higher temperatures incurred during combustion, it is very likely that polymerization of the oxygen-rich organic constituents would occur within the residence times of our experiment—producing very highly viscous material that may not permit rapid coalescence of individual bubbles within the droplets. Polymerization or liquid-phase pyrolysis to produce solids would also affect nucleation and bubble growth, as these processes have been shown to be affected by the presence of surfaces—filaments[40,42,48] and carbon particles.[49]

Comparison of Oak and Pine Oils. Under the same combustion conditions, pine oil displays the same stages of burning as oak oil: (a) quiescent burning, accompanied by a blue flame, in which the spherical shape of the droplet is not perturbed; (b) the microexplosion, accompanied by broadband luminosity, sudden expansion and distortion of the droplet, and release of fuel fragments; (c) coalescence of the droplet (due to surface tension) while burning in a faint blue flame, with the release of occasional small bright luminous bursts; and (d) the final stage of burning, which occurs in a yellow flame, indicating the presence of soot. The quiescent phase of burning lasts longer for the pine oil droplets than for the oak oil droplets—a result, perhaps, of the pine oil's lower viscosity, which would lead to a higher liquid-phase diffusivity and more rapid liquid-phase mass transfer.

Although the pine and oak oils behave similarly during combustion, differences are apparent during the microexplosion. As shown in Figure 6, droplets of oak oil behave fairly uniformly, usually releasing only tiny fragments of tens of microns or smaller. Droplets of pine oil, on the other hand, exhibit more variability, as

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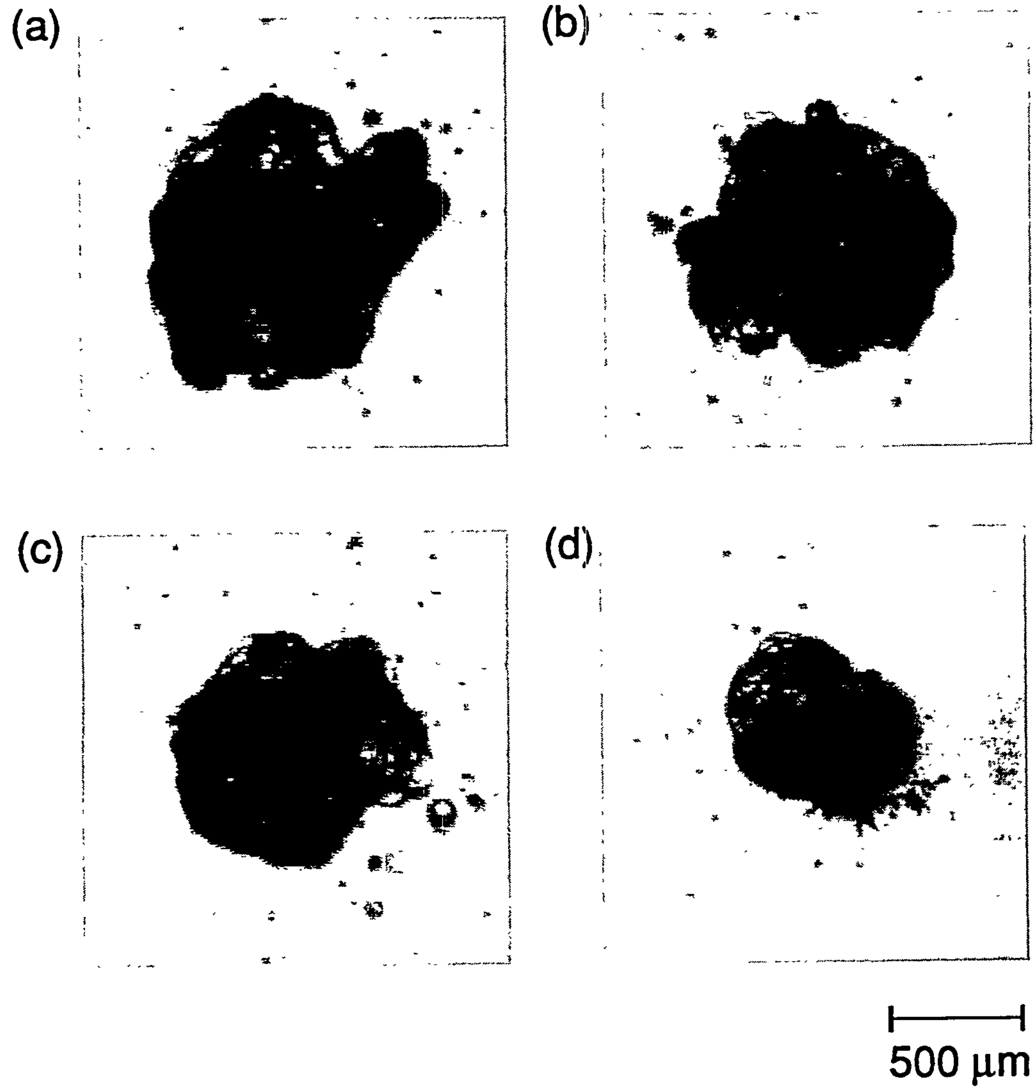

Figure 6. Video images of droplets of oak oil, microexploding while burning at 24 mol % O_2 in the BFCS reactor. Residence time of 34.8 ms.

shown in Figure 7. Swollen pine oil droplets often exhibit high transparency, as in Figure 7a—a property only rarely displayed by oak oil. Many microexploding pine oil droplets contract to one primary droplet, as those of oak oil, but many break into two or more fragments of appreciable size. Figure 8 displays droplet fragments observed at 64.9 ms, just 18 ms after the microexplosion. By this residence time, most of the fragments have assumed a spherical shape. The close proximity of these fragments ensures that they have all evolved from the same parent droplet since oil droplets are introduced into the reactor at >60 droplet diameters apart. Although we are not certain of the cause, the greater propensity of the pine oil droplets to fragment (compared to the oak oil droplets) appears to be due to differences in the viscosities of the two oils. The lower viscosity of the pine oil permits more rapid coalescence of gas bubbles within the oil droplet and more rapid transfer of the bubbles to the droplet's outer surface, where surface rupture occurs, resulting in droplet fragmentation. Other factors may have influence, however, *e.g.*, surface tension and the nature and quantity of the vaporizable components generated by the two oils at the time of microexplosion.

It should also be noted that despite the suspension-like character of the pine oil at room temperature, this oil displays solution-like behavior during combustion since it undergoes substantial swelling prior to the microexplosion, as reported for solutions.[34] It is likely that the suspended solids are soluble at the droplet temperatures achieved during combustion.

Droplet Size Distributions. More detail of the burning history of the biomass oil droplets is obtained from an analysis of the sizes of droplets recorded by video-imaging over the range of droplet residence times in the reactor. Figure 9 portrays oak oil droplet size distributions as a function of residence time in the BFCS reactor for the experimental conditions corresponding to Figure 5. When droplets are spherical, the droplet's diameter is used. For nonspherical droplets, an equivalent diameter is calculated from the square root of the product of the lengths measured along two axes of the droplet. Except for the data at 98.7 ms, each of the droplet size distributions in Figure 9 represents approximately 100 drops.

The droplet size distribution in Figure 9a depicts the monodisperse nature of the droplets generated in the BFCS. Within the quiescent burning regime (up to approximately 34 ms), the droplets stay spherical but swell slightly, as indicated by Figure 9b. This slight expansion of the droplet occurs despite the loss of droplet mass by fuel evaporation.

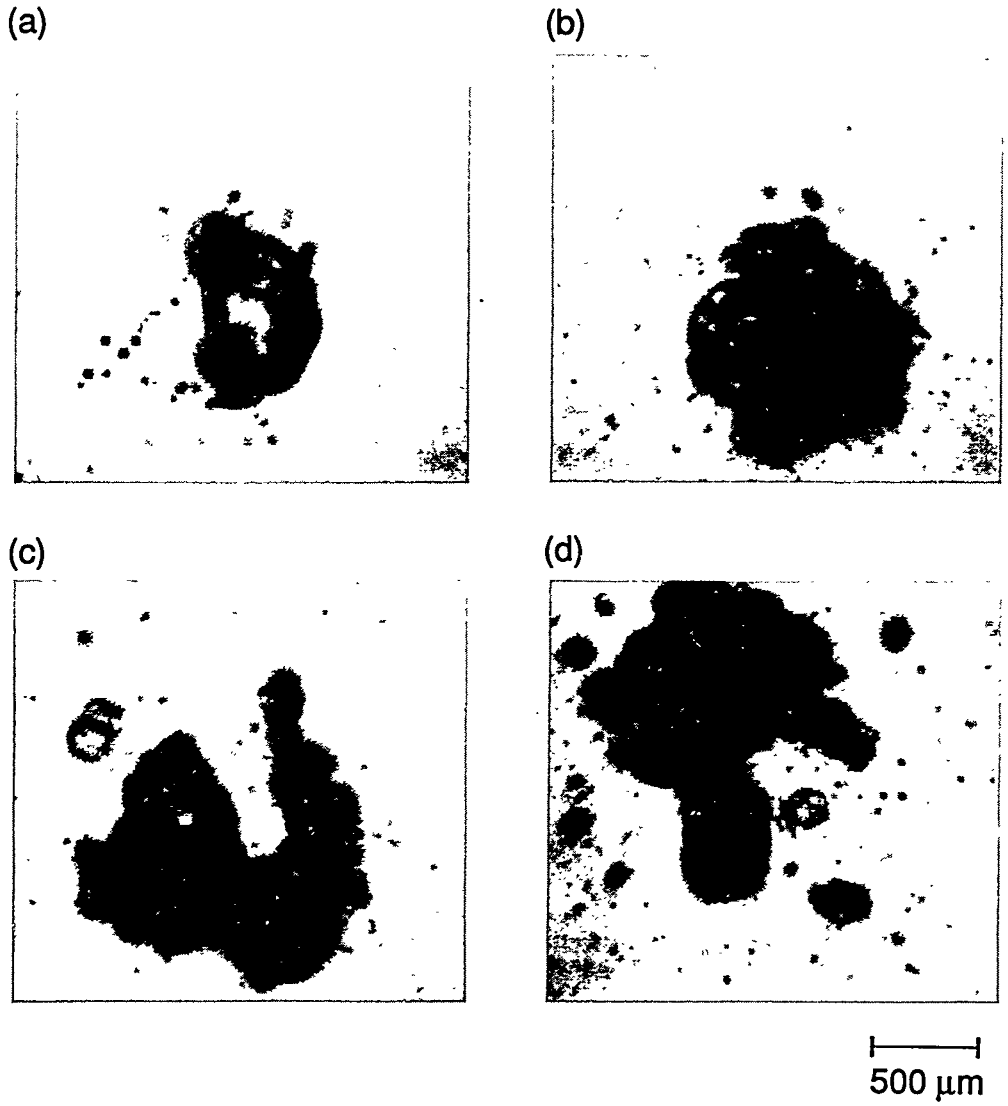

Figure 7. Video images of droplets of pine oil, microexploding while burning at 24 mol % O_2 in the BFCS reactor. Residence time of 47.2 ms.

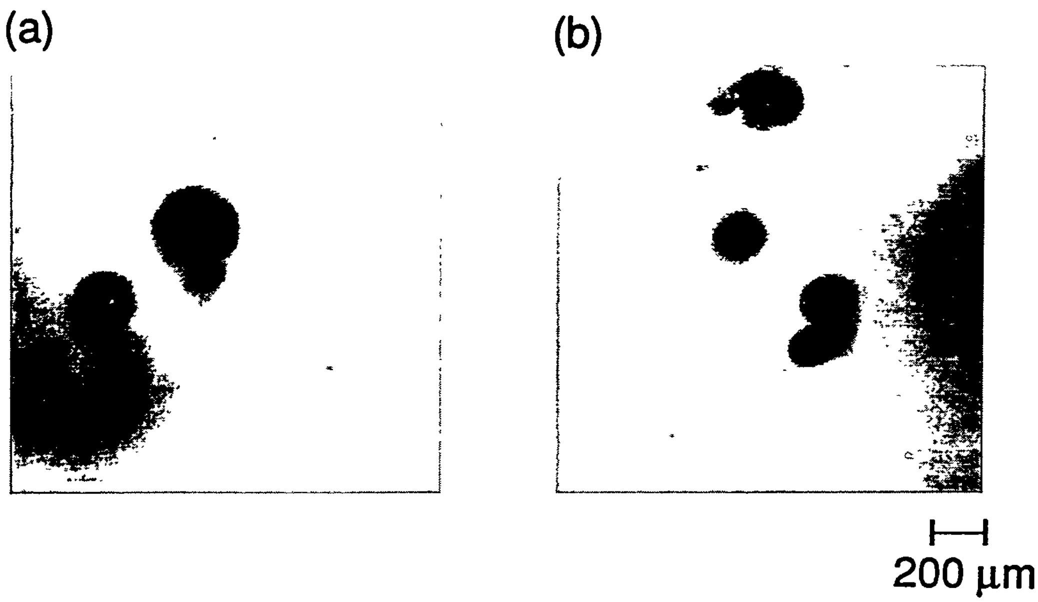

Figure 8. Video images of droplet fragments of pine oil, burning at 24 mol % O_2 in the BFCS reactor. Residence time of 64.9 ms.

Figure 9b shows that at 32.3 ms, a small proportion of oak oil droplets have undergone the sudden expansion that accompanies the microexplosion. The greatest number of droplets reach the microexplosion stage at 34.8 ms, however, as illustrated by Figure 9c. Figure 9, d and e, demonstrates the coalescence and gradual

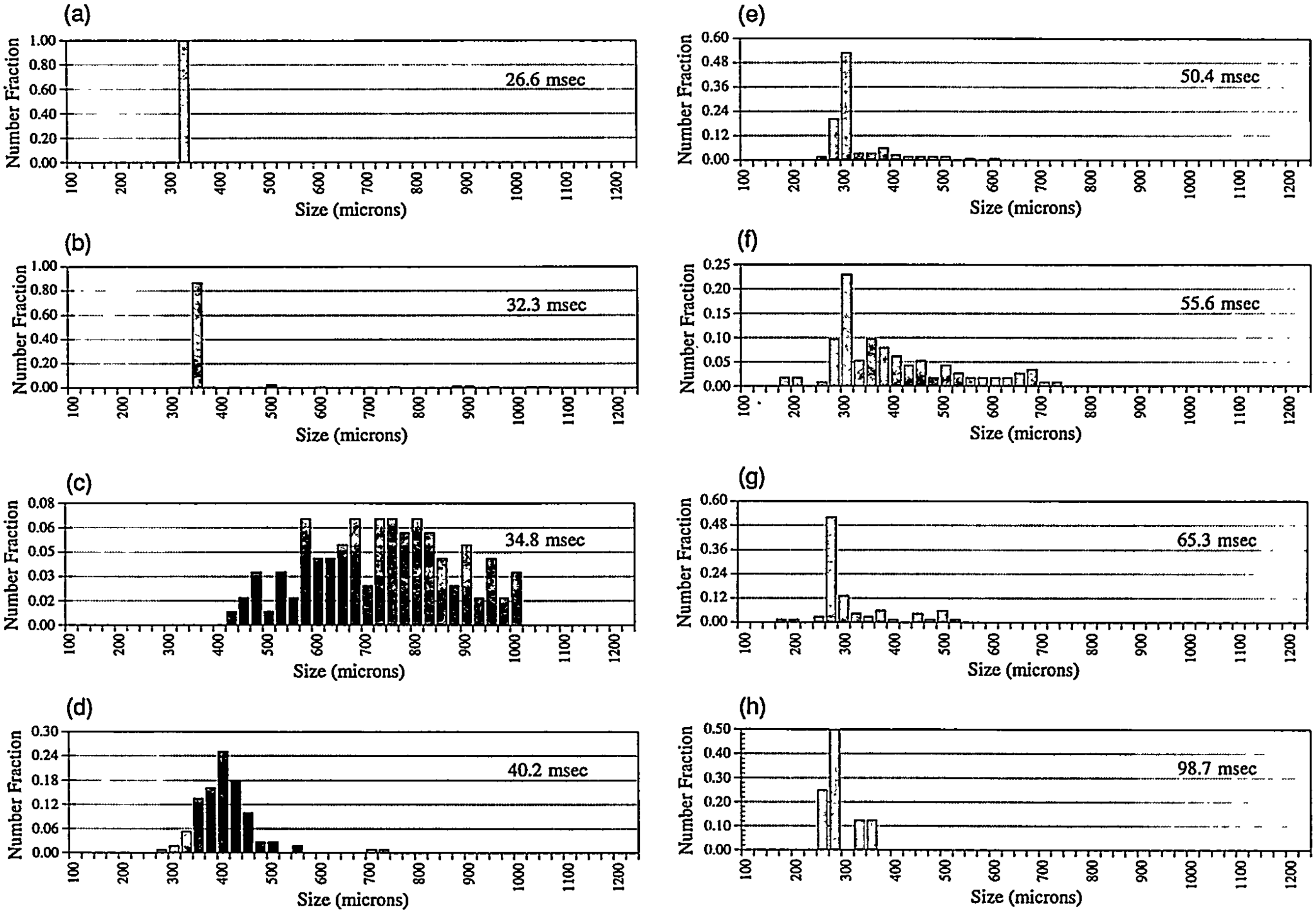

Figure 9. Size distributions of droplets of oak oil burning at 24 mol % O_2 in the BFCS reactor for (a) 26.6 ms; (b) 32.3 ms; (c) 34.8 ms; (d) 40.2 ms; (e) 50.4 ms; (f) 55.6 ms; (g) 65.3 ms; (h) 98.7 ms.

contraction of the droplets after they have undergone the microexplosion. The occurrence of larger droplets again at 55.6 ms (Figure 9f) coincides with the visual observation, at this residence time, of a secondary microexplosion, much smaller than the first one. Because during the primary microexplosion droplets do not expand or release vapor in exactly the same manner, postmicroexplosion droplets are not identical and the second microexplosion occurs over a broader range of residence times than the first. Following the secondary microexplosion, any subsequent bursts of fuel vapor release are of considerably smaller scale and are more erratic in timing. The fact that, at 98.7 ms (Figure 9h), droplets are still of an appreciable size indicates that even at the late stages of burning, oak oil droplets contain significant volumes of vapor.

The droplet size distributions of pine oil show the same trends in behavior as those of oak oil, with three minor exceptions: Pine oil swells less during the quiescent phase. During the microexplosion and afterward, droplet size distributions are shifted to slightly smaller diameters, reflecting the greater propensity of pine droplets to fragment during the microexplosion. The greater variability in the manner of the primary microexplosion of the pine oil droplets causes the second microexplosion of the pine oil droplets to occur over an even broader range of residence times than for the oak oil droplets.

Analysis of Biomass Oil Residues. All of the results presented above for the combustion of the biomass oils come from experiments performed in an environment of 24 mol % O_2, where the microexplosion and full burnout of the oak oil occur at 34.8 and 149 ms, respectively. An increase in O_2 concentration to 29% speeds up the entire combustion process: The microexplosion occurs at 26.6 ms, and full burnout occurs at 113 ms. At 19 and 14 mol % O_2, full burnout of oak oil does not occur within the residence times of the BFCS reactor, and the microexplosion is delayed to 40.2 and 53.2 ms, respectively. Similar results are found for pine oil. Under these conditions, all phases of droplet combustion are retarded, and solid residues are found in the reactor exhaust. Representative solid residues from biomass oils are portrayed in Figure 10, SEM photographs of solids produced from pine oil at 14 mol % O_2 and manually extracted from the exhaust stream of the BFCS reactor. As shown in Figure 10a, the solid residues in these experiments are of two types: dense, glassy spheres and fragile, thin-walled cenospheres. As the SEM photograph in Figure 10b reveals, the glassy spheres contain cavities that indicate the existence of vapor pockets within these spheres at the time of their hardening. EDS analysis of the glassy-type solids reveals that they are composed of C and O, in a mass ratio of approximately 4 to 1. Most of the material in these solids dissolves in methanol, so they have retained the polar character of the parent fuel and have not yet undergone severe carbonization. There are small amounts of insoluble residue left behind, however, that signify the initial stages of carbonization.

EDS analysis of the cenosphere-type residues reveals a C to O mass ratio of approximately 9 to 1 in these

(a)

(b)

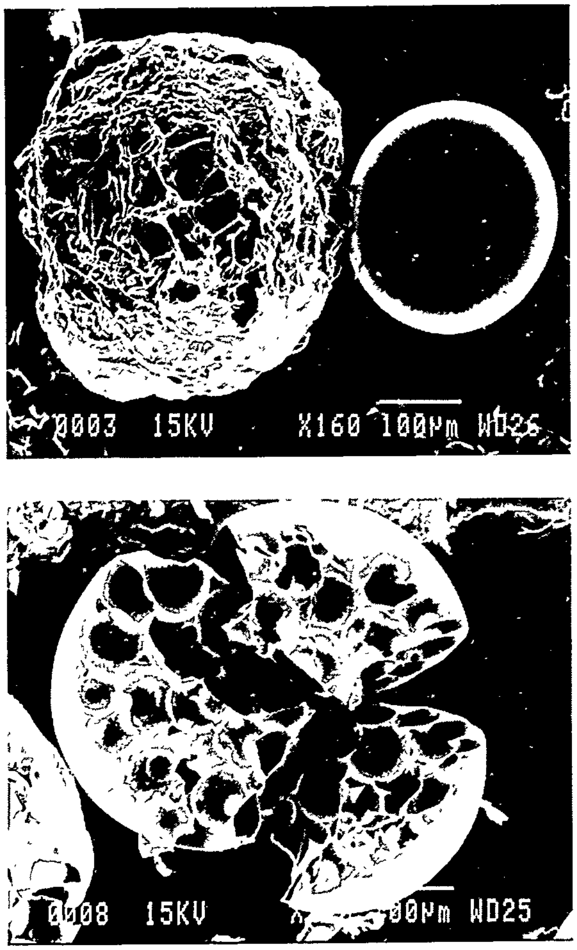

Figure 10. Scanning electron micrographs of solids produced from pine oil during burning at 14 mol % O_2 in the BFCS reactor: (a) cenosphere and glassy types; (b) interior of a glassy type.

materials. Consistent with their lower oxygen contents, these solids do not dissolve in methanol. Nor do they dissolve in dichloromethane, a solvent for aromatic materials. They therefore appear to result from a later stage of combustion than the dense glassy residues—a stage in which carbonization has taken effect. This conclusion is consistent with the fact that residues, collected at the same time, from combustion at 19 mol % oxygen contain a higher proportion of cenospheres than the residues from 14 mol % oxygen.

The oak oil produces the same types of solid residues as the pine oil, as illustrated in Figure 11, SEM photographs of residues from oak oil combusted at 19% oxygen. Figure 11, a and b, depicts three glassy solids and one cenosphere before and after gold-coating, respectively. The oxygen-rich dense solids, if uncoated, are susceptible to charging and prove to be unstable under the electron beam of the scanning electron microscope. After gold coating, however, the images of the oxygen-rich dense solids are sharpened, due to the cessation of the charging phenomenon associated with these polar solids. The carbon-rich, oxygen-deficient cenospheres, on the other hand, exhibit stability under the electron beam and show no evidence of charging. The cenospheres are mechanically fragile, as evident from the collapse of the one in Figure 11a,b, as a result of the evacuation step of the gold-coating procedure. The thin nature of the cenosphere membrane (~0.2 μm), portrayed in Figure 11c, partially accounts for this fragility.

(a)

(b)

(c)

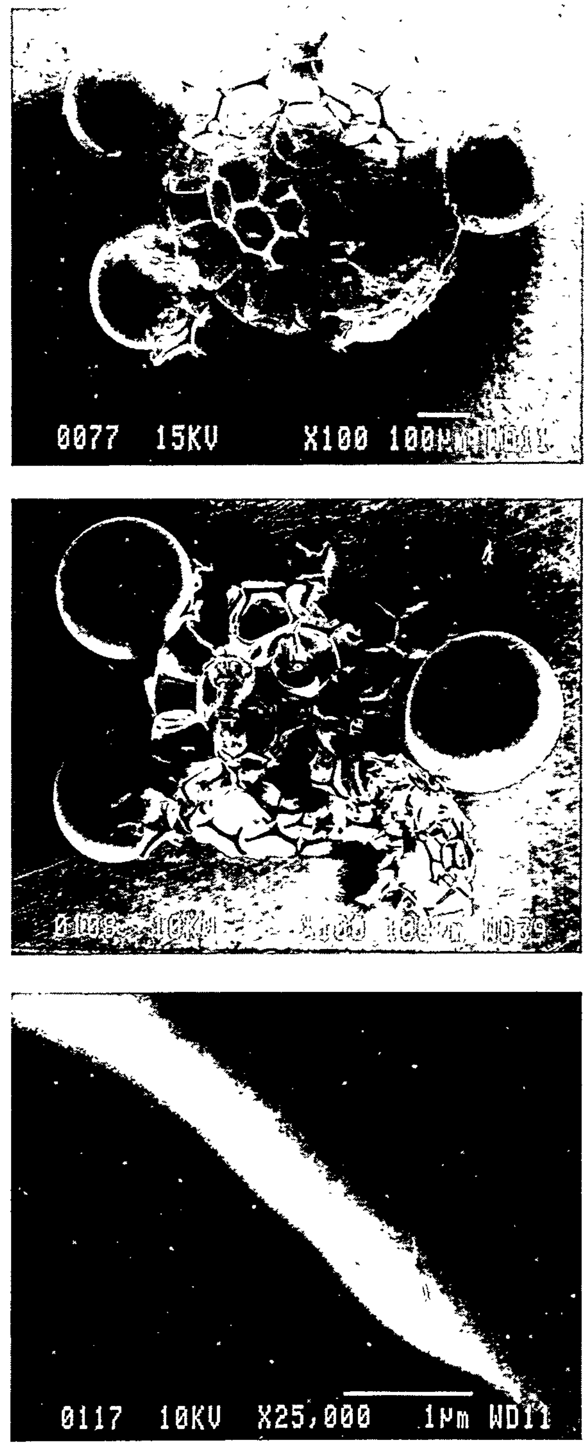

Figure 11. Scanning electron micrographs of solids produced from oak oil during burning at 14 mol % O_2 in the BFCS reactor: (a) three glassy type and one cenosphere type before gold coating; (b) three glassy type and one cenosphere type after gold coating; (c) close-up of a light-colored cell membrane of the cenosphere residue in (b).

Evident from Figure 11a,b is the cellular nature of the biomass oil cenosphere structure, a structure similar to those displayed in the char of a softening bituminous coal[50] and in the partially oxidized residue of a bitumen-in-water emulsion droplet.[51] The cells resemble those associated with Marangoni convection, which results from local gradients in surface tension.[52-54] The mul-

(50) Fletcher, T. H.; Hardesty, D. R. *Compilation of Sandia Coal Devolatilization Data*; SAND92-8209 UC-362, May, 1992.
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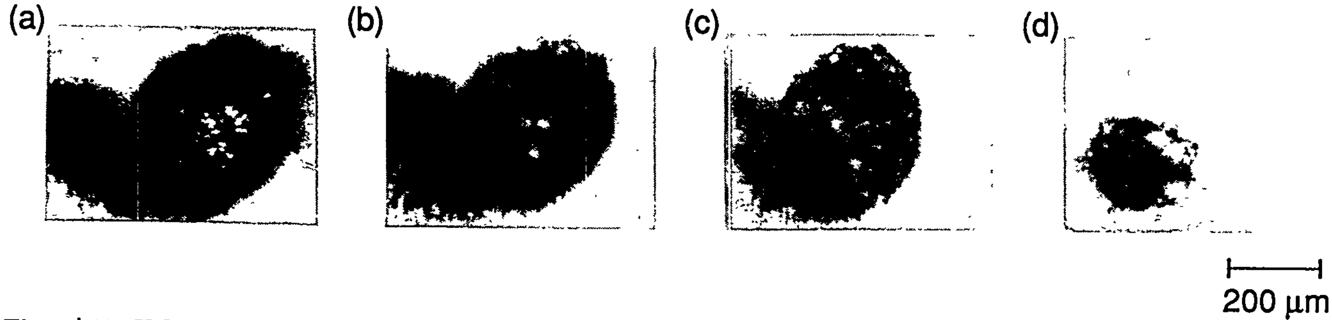

Figure 12. Video images of an oak oil cenosphere type residue burning in the CPI flow reactor at 6 mol % O_2. Residence times of (a) 0 s; (b) 0.52 s; (c) 0.58 s; (d) 0.93 s.

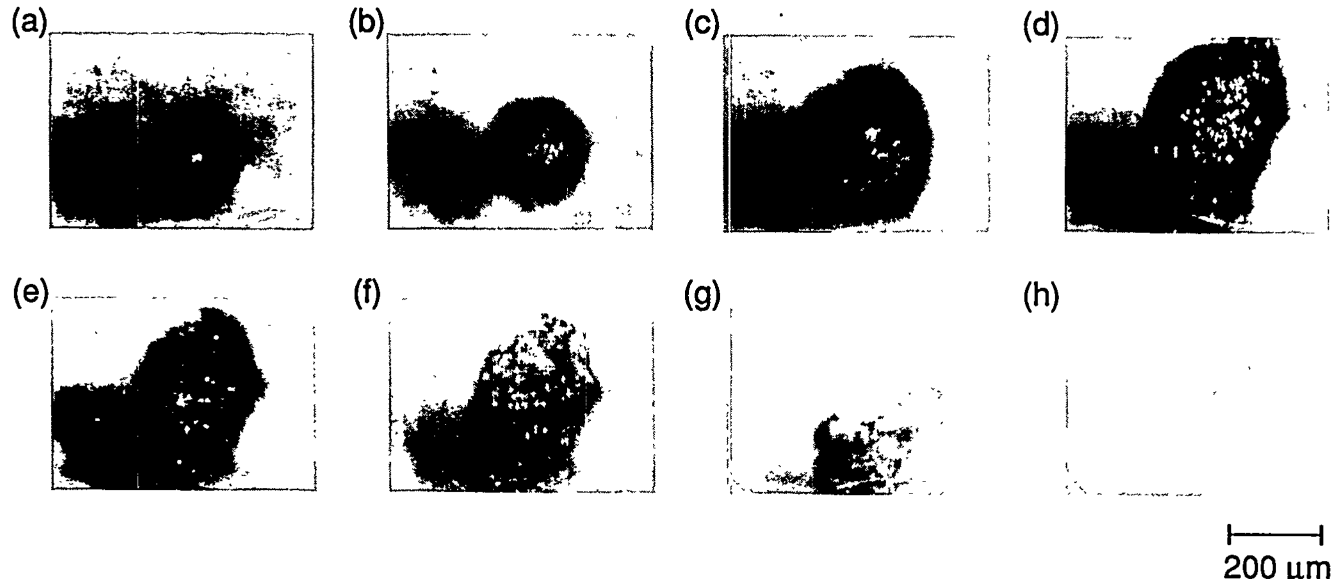

Figure 13. Video images of a pine oil glassy residue burning in the CPI flow reactor at 6 mol % O_2. Residence times of (a) 0 s; (b) 0.13 s; (c) 0.20 s; (d) 0.30 s; (e) 0.90 s; (f) 1.07 s; (g) 1.40 s; (h) 2.17 s.

ticomponent nature of the biomass oils, coupled with the carbonization transformations occurring in these materials at the latter stages of combustion, may be responsible for such local gradients. EDS analysis of the darker regions bordering the cells in Figure 11 shows them to be mostly carbon (C to O mass ratio of 19), whereas the lighter colored cell membranes are higher in oxygen (C to O mass ratio of 2). Figure 11c suggests that the material comprising these cell membranes is very smooth and glassy, similar to the glassy carbons produced by the polymerization of oxygen-rich furfuryl alcohol.[55] The thin, oxygen-rich nature of this membrane material would most probably make it more susceptible to oxidation than the more carbon-rich border regions.

It is interesting to note that the biomass oil cenospheres bear no resemblance to the rough, porous, nonglassy cokes produced during the combustion of residual oils from petroleum.[41,56,57] Whereas the cokes from petroleum-based oils arise from the liquid-phase pyrolysis and polymerization of hydrocarbon-rich, oxygen-deficient petroleum constituents,[48,58,59] the biomass oil residues arise from the thermally induced pyrolysis and/or polymerization of oxygen-rich organic material.

Combustion of Biomass Oil Residues. Figure 12 depicts the burning, within the CPI reactor, of a cenosphere-type residue produced from combustion of oak oil at 14 mol % O_2 in the BFCS reactor. As predicted, the thin, oxygen-rich membranes comprising the cells are the first material to be depleted. The carbon-rich skeleton then slowly burns away, leaving no observable residue.

Figure 13 reveals the different stages of combustion of a glassy sphere residue of pine oil, collected after burning in 14 mol % oxygen in the BFCS reactor. Upon heating, the glassy sphere rapidly expands to the cenosphere-type residue, which retains its skeletal structure throughout subsequent burning until no detectable residue exists. The absence of any noticeable ash, after combustion of the residues, is consistent with the fact that no inorganic elements are detected by EDS in the uncombusted oil residues. The transformation, during combustion, of the glassy sphere to the enlarged cenosphere is also consistent with the earlier observa-

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tions, related to oxygen content and solubility, that indicate that the glassy spheres are precursors to the cenospheres and that the combustion of the cenospheres is the final step of biomass oil droplet combustion. This finding accounts for the observation that at the later stages of combustion in the BFCS reactor, the biomass oil "droplet" diameters, obtained by *in-situ* imaging, maintain an appreciable size until full burnout. The transformation of the glassy-type residue into the swollen cenosphere parallels the plasticizing behavior of softening bituminous coals and accounts, perhaps, for the similar cellular appearance of the biomass oil cenospheres and the bituminous coal pyrolysis product char of Fletcher.[50]

Conclusions

Single droplet experiments with No. 2 fuel oil and oak and pine oils highlight several contrasts in the combustion behavior of these multicomponent fuels. For No. 2 fuel oil, efficient mass transfer within the droplet (related to the fuel's low viscosity) and the fuel's narrow range of component volatilities lead to quiescent burning throughout the droplet's lifetime. The hydrocarbon-rich, oxygenate-deficient nature of the No. 2 fuel oil's components facilitates soot production in the fuel vapor cloud surrounding the droplet. No coke or solid residues are found from the droplets themselves.

In contrast, the biomass oils initially burn quiescently, free of soot, in a blue flame, indicative of volatile oxygenated components. The broad range of component volatilities and inefficient mass transfer within the viscous biomass oils bring about an abrupt termination of the quiescent stage, however, at about a quarter of the way into the droplet's lifetime. Vapor suddenly builds up within the droplets, causing rapid swelling and distortion, followed by surface rupture and the release of fuel fragments. Droplet coalescence follows, and subsequent burning occurs in a faint blue flame with occasional smaller scale releases of bursts of vapor. At the late stages of biomass oil combustion, droplets are accompanied by clouds of soot, produced from the gas-phase pyrolysis of fuel vapor. Liquid-phase polymerization and/or pyrolysis of the oxygenate-rich biomass oils leads to the formation of carbonaceous cenospheres, whose burnout signifies the final stage of biomass oil droplet combustion. Oak and pine oils behave very similarly during combustion, though differences in their physical properties cause pine oil to show more variability during the microexplosion and more susceptibility to fragmentation. Changes in oxygen concentration alter the timing of the events during biomass oil combustion, but not their nature.

Despite large differences in fuel properties and combustion mechanisms, the burning times of the biomass oils and No. 2 fuel oil are fairly comparable—those of the biomass oils about 10% longer under our experimental conditions. This finding underlines the importance of the microexplosion in dispersing the biomass-derived fuel into the oxidizing environment.

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Baseline NO_x Emissions During Combustion of Wood-Derived Pyrolysis Oils

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ABSTRACT

NO_x emissions from two pyrolysis oils of similar origin and overall composition but differing nitrogen contents (0.12 and 0.32 % of dry fuel) are determined in a pilot-scale combustor. No NO_x reduction technology is employed in these tests, establishing the baseline or uncontrolled levels of NO_x. Measured effluent oxygen concentrations range from near 0% to near 21%, with stoichiometric ratios ranging from 0 to 1. NO and NO_x are measured separately and found to differ by insignificant (≈10-25 ppmv) amounts. Other relevant gas species (CO_2, CO, total hydrocarbons, and O_2) are also reported.

Peak NO_x emissions from these fuels vary from about 300 to around 650 ppmv, with lower levels associated with low nitrogen content fuels. Trends with stoichiometric ratio and fuel nitrogen content agree qualitatively with behavior from other nitrogen containing fuels, including biomass, coal, and petroleum oils. Nitrogen conversion efficiencies as a function of stoichiometric and fuel nitrogen content are observed to decrease with increasing fuel nitrogen content and increase with increasing oxygen content. Measurements of thermal, prompt, and fuel NO_x contributions indicate that fuel NO_x is the dominant formation mechanism for these fuels. These data suggest that NO_x formed during combustion of pyrolysis oil lends itself to many of the same control technologies as are used in other nitrogen-containing fuel.

INTRODUCTION

The combustion behavior of biomass-derived pyrolysis oils under conditions similar to those found in commercial boilers is largely uncharacterized. One of the major issues associated with such combustion is the production of pollutants. Of primary interest is the production of NO_x. Since such oils are ultimately targeted toward both boiler and turbine applications, NO_x production under a wide range of stoichiometries is of concern.

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[1]On sabbatical leave from University of California, Davis Department of Biological and Agricultural Engineering.

The nitrogen-containing, combustion-generated compounds of greatest concern are nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O). The term NO_x generally refers to the former two compounds or, when used more broadly, to all three. NO is the most studied and, in most cases, the most significant of the three compounds. Equilibrium NO concentrations depend on both temperature and stoichiometry. At flame temperatures (2000 K), equilibrium values of NO range from about 3000 ppmv at an equivalence ratio of 0.8 to about 30 ppmv at an equivalence ratio of 1.2 [Bowman, 1991]. At exhaust temperatures (300 K), equilibrium concentrations of NO are uniformly less than 10 ppmv. Exhaust NO emissions from combustion systems are rarely as high as their equilibrium value at the flame temperature, but are generally higher than their equilibrium value at the exhaust temperature, indicating that both NO formation and destruction are influenced by chemical kinetics.

Formation mechanisms for NO_x are generally divided into three categories: thermal NO_x, fuel NO_x, and prompt NO_x. Each is discussed here in terms of the NO, which is typically the most significant component of NO_x. Thermal NO has the most completely understood mechanism from a chemical kinetic viewpoint. It depends on the relatively slow (slow compared to most combustion reactions) conversion of molecular or atomic nitrogen to NO by oxygen and hydroxyl radicals. The formation of thermal NO is strongly dependent on temperature, moderately dependent on oxygen concentration, and nearly independent of pressure.

Nitrogen-containing fuels produce nitrogen-containing radicals in flames that can greatly increase the amount of NO observed in the vitiated flow by the fuel NO_x mechanism. Fuel-bound nitrogen is generally considered to generate some gas-phase intermediate species (HCN or some derivative is most commonly cited) that competitively reacts to form either molecular nitrogen or NO. The details of the kinetics are less well understood than those of thermal NO formation, but parametric studies indicate general trends. NO levels increase with increasing fuel nitrogen contents, but the dependence is less than first order. Therefore, the *fractional* conversion of fuel nitrogen to NO generally decreases as the amount of fuel nitrogen increases even though the *total* amount of NO increases with increasing fuel nitrogen [Pohl and Sarofim, 1976]. Most studies conclude that the form of nitrogen in the parent fuel has little impact on NO concentrations [Bowman, 1992], although most of the work appears to have been performed on aromatic compounds not containing amine functional groups. Biomass-bound nitrogen is believed to occur in amine form to a much greater extent than in other fuels (notably, petroleum-derived oils and coal). If pyrolysis conditions are sufficiently moderate to prevent conversion of amine nitrogen to other forms, the fate of the amine nitrogen during combustion may be quite different in the biomass-derived pyrolysis oils than that of nitrogen from other fuels.

Prompt NO is the final mechanism for NO formation. Prompt NO refers to near-flame concentrations of NO that are higher than can be explained by the thermal mechanism alone. Proposed mechanisms for prompt NO formation involve both hydrocarbon radical intermediates and oxygen or hydroxyl radicals [Bowman, 1991]. The mechanism involving hydrocarbon intermediates has many similarities with that of fuel NO.

Other forms of NO_x (NO_2, N_2O) contribute to the total emission. NO_2 is formed at relatively low temperatures, and is rapidly reconverted to NO at high temperatures (lifetime of ≈ 10 ms @ 1500 K). N_2O is also a low-temperature species, with lifetimes shorter than those of NO_2 at higher temperatures. Most recent measurements indicate that NO_2 is a minor component of conventional, high-temperature combustion systems [Bowman, 1992].

The critical engineering issues in NO_x formation from pyrolysis oils are the overall NO_x emissions and their sensitivity to combustion of specific types of pyrolysis oils as well as operating conditions. In most of the results reported below, total NO_x, rather than NO, is reported. In these cases, the measurements are performed by passing the sampled effluent from the MFC through a catalytic device that reduces NO_2 to NO. The concentration of NO is measured after this conversion. Bypassing the converter renders an NO, as opposed to NO_x, measurements. We occasionally bypass the converter to record the difference between NO and NO_x measurements. In these data, the difference amounted to up to 30 ppmv. This difference is negligible for the purposes of our discussion below. The sampling system has been described in earlier reports. Calibration gases are introduced in this system at the probe tip, not the analyzers, to verify that reactions on sampling system surfaces do not influence the results.

EXPERIMENTAL APPROACH

Concentrations of NO, NO_x (as NO_2), SO_2, CO, total hydrocarbons (THC as CH_4), CO_2, and O_2 were monitored by continuous analyzers sampling the exit gas from Sandia's Multifuel Combustor (MFC). This laboratory unit is designed to simulate commercial-scale combustion furnaces, but is highly instrumented with diagnostics and controllers to provide detailed characterization of gas compositions and reactions, solids reactions, and surface interactions. The combustor, depicted in Figure 1, is a 4.2 m high vertical turbulent-flow furnace with a 15 cm inner diameter. The upper six of seven furnace modules are electrically heated and independently controlled. The furnace duct is open at the bottom, and discharges across a 0.7 m high open space into the inlet of a large duct, which also draws laboratory air for dilution and cooling prior to exhaust. For the purposes of emissions monitoring, a sampling probe is inserted into the undiluted and uncooled exhaust gas through the lowest furnace section below the fuel injection point. A natural gas burner situated at the top of the furnace can supply a preheated, vitiated oxidant flow to aid in simulating full-scale furnace conditions or to compare gas compositions from non-nitrogen containing fuels (methane or natural gas) with those from nitrogen-bearing fuels. NO_x emissions in the electrically heated flow, without combustion of pyrolysis oil or natural gas, were below 10 ppmv with the furnace wall and exit gas temperatures at 900°C. Under the same operating conditions, but with a natural gas flame, NO_x emissions were between 30 and 40 ppmv. By comparison, peak NO_x concentrations for the pyrolysis oils tested here ranged from 250 to 650 ppmv.

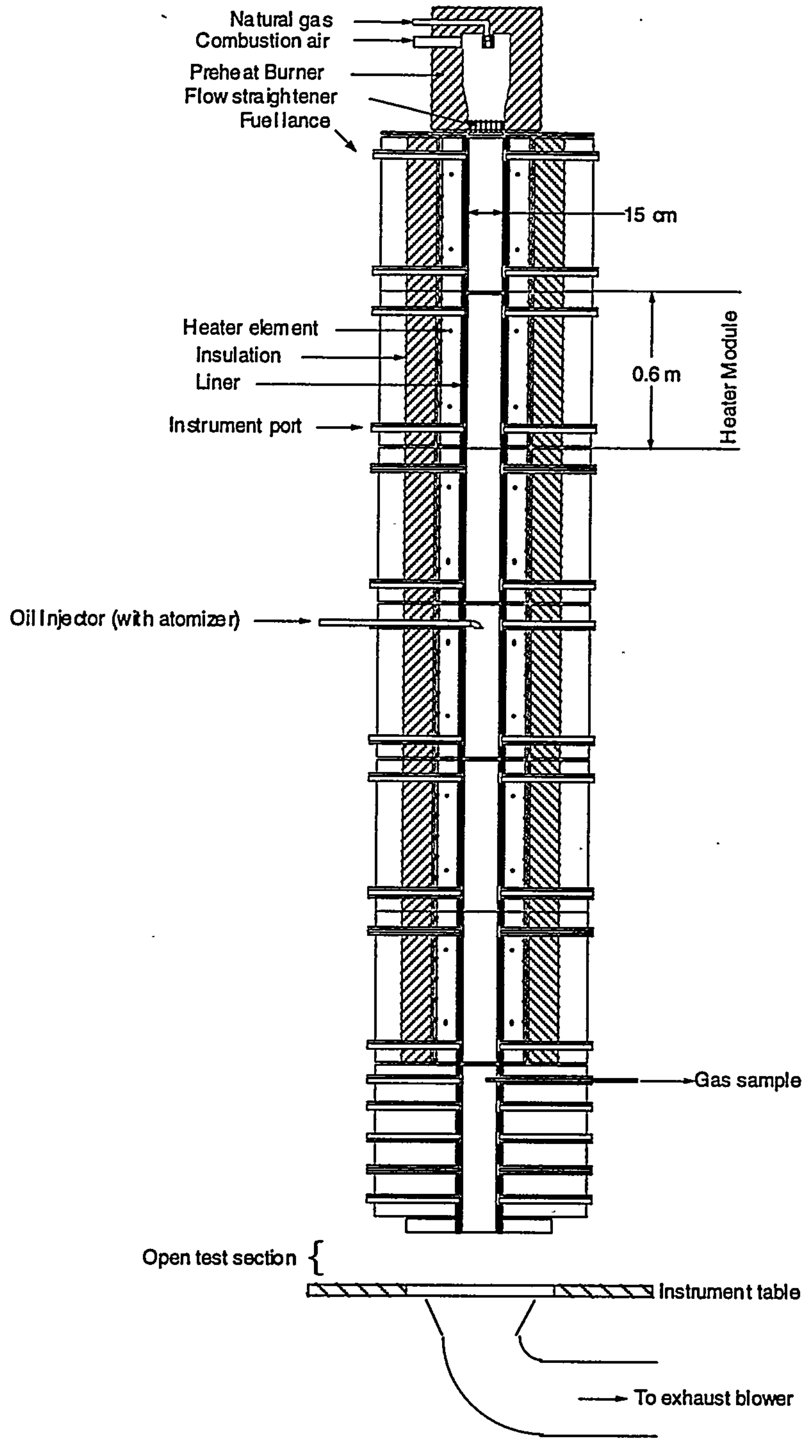

Figure 1 Schematic diagram of Sandia's Multifuel Combustor as used in these studies of pyrolysis oils.

CO_2, CO, NO, NO_x, and SO_2 concentrations are measured using nondispersive infrared (NDIR) analyzers, O_2 concentrations by a paramagnetic analyzer, and total hydrocarbons (THC) by a flame ionization detector. The maximum CO concentration that could be measured was 1,000 ppmv, which was exceeded in many cases when approaching an equivalence ratio of unity. All concentrations were measured on a dry gas basis. The instrumentation is calibrated before and usually after each run by introducing calibration gases at the sample probe tip. No interferences between measured species are evident in either the calibration or the instrument characterization tests. All gas concentrations were measured on a dry-gas basis, with water removed by refrigeration. Sample lines are heat traced up to the refrigeration point to avoid condensation on the teflon sample train walls.

FUEL CHARACTERISTICS

The oil used to generate all of the data reported below was produced by Ensyn Technologies Inc., Greely, Ontario, Canada and were provided to Sandia by NREL. A dry, hardwood feed stock was used to produce the oil. The properties of this pyrolysis oil are clearly distinguished from those of traditional fuel oils, such as petroleum distillates. The presence of significant water in the liquid pyrolysis products disqualifies them as oils by some strict definitions [Lapedes, 1978]. They occasionally exhibit strong acidic tendencies and often contain some suspended solids, neither of which properties are common in traditional oils. Although reference to these fuels is made here and elsewhere as pyrolysis oils, these chemical differences play significant roles in their handling and some combustion properties.

Table 1 indicates the relevant properties of these pyrolysis oils. Compared with traditional petroleum-derived oils, the pyrolysis oils contain much more moisture, oxygen, and ash, comparable amounts of nitrogen, sulfur, and hydrogen (dry basis), and have about half of the heating value.

Table 1 Properties of the Ensyn Pyrolysis Oils Relevant to NO_x Emission Studies (dry basis)

	Oil #1	Oil #2
Moisture	25	27
C	59.23	58.64
H	10.25	10.07
O	29.10	29.21
N	0.32	0.12
S	0.05	0.01
Ash	1.05	1.05
Heating Value, daf MJ/kg (BTU/lb)	23.1 (9888)	23.0 (9919)

RESULTS

The focus of our work and the bulk of the discussion is on NO_x generation. A brief report of other major gas species is included after the discussion of NO_x.

NO_x Emissions

Combustion tests of the low-nitrogen content oil (Ensyn pyrolysis oil #2) produced the data that are reported in Fig. 2 on both an as-measured and corrected basis. As the overall stoichiometry changes, the concentration of NO_x varies in part due to changing combustion temperatures and kinetics and in part due to the dilution of the vitiated flow by changing ratios of fuel to air. The data are corrected to remove the latter effect by normalizing the measured value of NO_x. The normalization results in the concentration of NO_x that would have been produced had the combustor been fired at some arbitrary excess oxygen level. There is no general agreement on what oxygen concentration should be chosen for this normalization. We report the data on a 3% O_2 basis – the same basis on which many pollutant emission regulations are based.

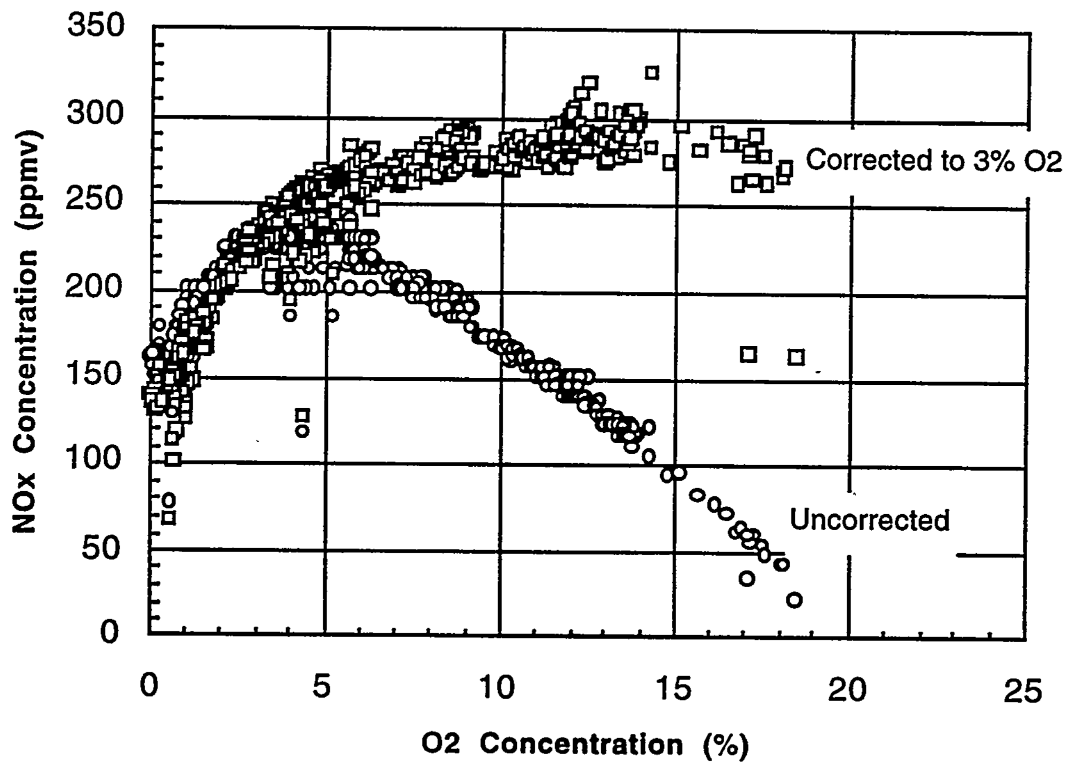

Figure 2 Measured NO_x emissions from the Ensyn 1 pyrolysis oil fired in the MFC as a function of measured effluent oxygen concentrations.

Another common basis for reporting such data is the calculated equivalence ratio based on complete combustion of the reactants. As the equivalence ratio approaches unity, the calculated amount of O_2 in the vitiated flow assuming complete combustion may differ significantly from the actual value due to the formation of CO or other partially oxidized species.

The data indicate a rapid increase in NO_x with increasing oxygen concentration in the oxygen mole fraction range of 0 to about 2 %. At oxygen concentrations greater than about 2%, the raw data indicate a monotonic decrease in NO_x emissions with increasing oxygen concentration. This trend is due almost entirely to the dilution of NO_x by increased combustion air. When corrected for the dilution effect, the NO_x levels are seen to stabilize, with essentially no change with increasing oxygen concentration. Both of these observations are consistent with the combustion of other nitrogen-containing fuels. The initial increase represents the increased formation of NO_x with increasing availability of oxygen in the flame zone. At some point, the formation of NO_x becomes independent of oxygen concentration (large excess oxygen), therefore the only changes in NO_x concentration noted with increasing O_2 are the dilution effect.

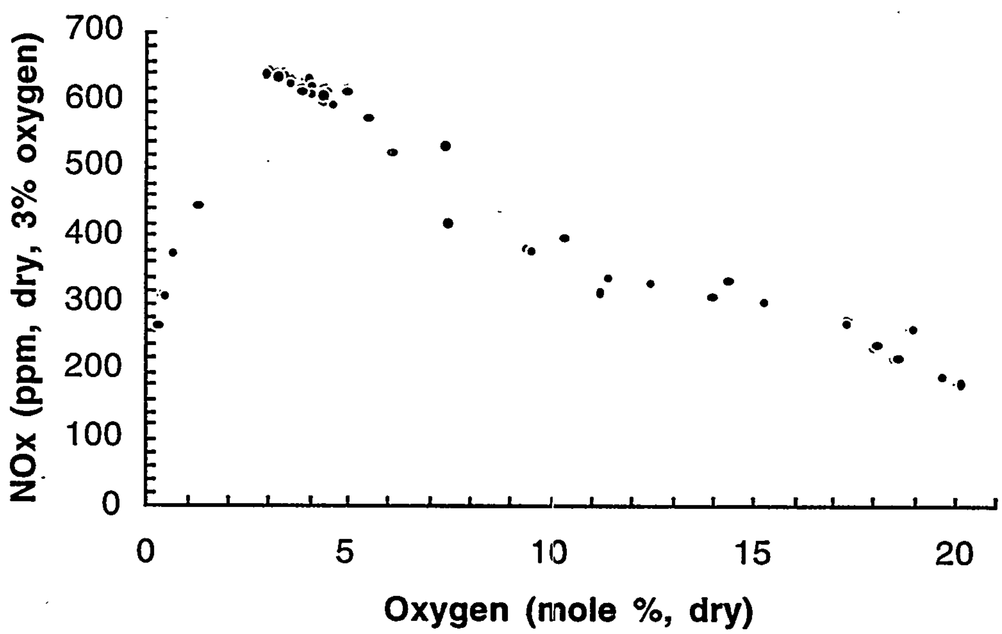

Figure 3. NO_x concentrations (normalized to 3% O_2) from combustion of the high-nitrogen content pyrolysis oil in the MFC.

Data from the high-nitrogen content fuel (Oil #1) are illustrated in Fig. 3 and do not exhibit the plateau in NO_x concentrations at high oxygen concentrations seen in Fig. 2. In the

experiments with Oil #1, flame temperatures changed significantly as we changed oxygen concentrations because the atomizing air ratio was changed significantly. In the experiments with Oil #2, effluent oxygen concentration was changed by changing the secondary air, which has little influence on the temperature and stoichiometry of the flame. Therefore, flame temperature did not change significantly.

Other qualitative results are also consistent with data from combustion of other nitrogen-containing fuels. For example, NO_x concentrations were also measured in the MFC at the same gas temperature ($\approx$ 1000 °C) but with no combustion of pyrolysis oil or any other fuel (temperature rise was achieved through electrical heating). NO_x levels under these conditions were uniformly less than 10 ppmv. NO_x concentrations measured during the firing of natural gas at the same overall temperature were uniformly less than 40 ppmv. The increase relative to electrical heating is presumed to be associated with the generation of radicals in the flame, which increases the generation of NO_x in the combustion zone. These results suggest that thermal NO_x makes only insignificant contributions to the overall NO_x concentrations observed in the gases. This, too, is consistent with results from other nitrogen-containing fuels.

Similarly, the quantitative results do not differ greatly from data on the combustion of other fuels. For example, uncontrolled NO_x emissions from coal- and oil-fired power plants operating with about 3% oxygen in the flue gas and with nitrogen concentrations in the fuel of about 0.4 % result in NO_x emissions of approximately 700 ppmv. However, peak temperatures in both coal and petroleum-oil flames exceed those in the pyrolysis oil flames by several hundred Kelvins. Since NO_x emissions increase with increasing temperature, these results suggest that pyrolysis oils tend to form slightly more NO_x than other similar fuels, all else being equal.

A major difference between the results from Ensyn Oil #2 and those from Ensyn Oil #1 is the peak NO_x concentration. This is related to the amount of fuel nitrogen in the oils. As indicated in Table 1, the fuel nitrogen level in Ensyn Oil 1 is about 2.7 times greater than that of Ensyn Oil 2. The observed increase in peak effluent NO_x concentration is consistent with this change in fuel nitrogen. However, the NO_x concentrations do not increase in proportion to fuel nitrogen content. The peak NO_x concentration measured in our combustion tests increases by a factor of about 2, whereas fuel nitrogen content increases by a factor of 2.7. This, too, is consistent with trends from other nitrogen-bearing fuels.

Other Major Gas Species

Changes in other major gas-phase species were also recorded during these tests. Figure 4 illustrates the CO concentration as the combustor stoichiometry approaches an equivalence ratio of unity. CO concentration increases from negligible to about 1%, with the highest measured values occurring the lowest measured oxygen concentrations (about 0.7 % oxygen). These conditions correspond essentially to an equivalence ratio of 1 (i.e., all of the excess oxygen would be consumed if the CO were to convert to CO_2). The abscissa in Figs. 2 through 4 represents measured O_2 concentrations, not calculated values based on flow rates.

Increases in CO concentrations correspond closely to the observed decreases in NO_x concentrations. Both reflect the competition between species for oxygen as the available oxygen becomes limited. The conversion of carbon to CO is relatively rapid and decreases the amount of oxygen available for NO_x formation. However, the conversion of CO to CO_2 is relatively slow and, in the presence of a limited oxygen supply, CO concentrations are appreciable.

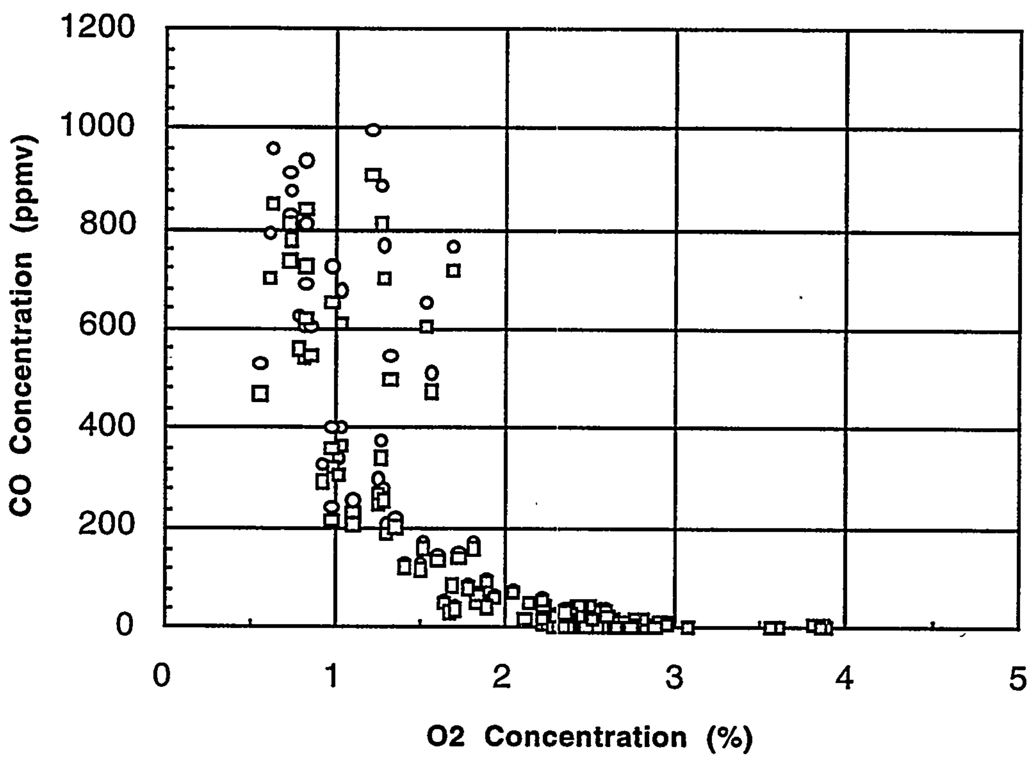

Figure 4 CO concentration as a function of measured oxygen concentration in the MFC during combustion of a pyrolysis oil. Squares represent corrected values. Circles represent uncorrected vlaues. Correction to 3% oxygen makes little difference over the limited range of oxygen concentrations with measureable CO concentrations. Compare with Figs. 2 and 5.

Figure 5 illustrates the trend in observed CO_2 concentrations with changing oxygen concentrations. The only significant trend is the effect of correcting the data to 3 % O_2. There should be small decreases in the CO_2 concentrations associated with the changes in CO concentration illustrated in Fig. 4, but the changes in CO_2 are insignificant ($\approx$ 1 %) compared to the overall CO_2 concentration (16 %).

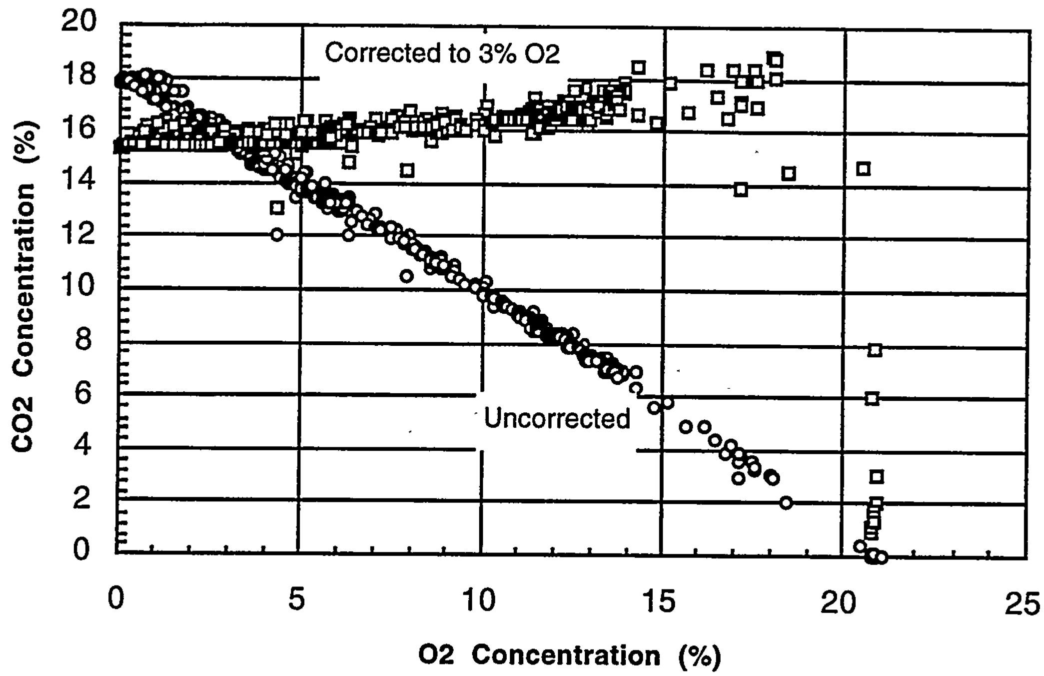

Figure 5 CO_2 concentration as a function of measured oxygen concentration in the MFC during combustion of Ensyn pyrolysis oil #2. Compare with Figs. 2 and 3.

These results suggest that NO_x controls used for other nitrogen-containing fuels will work with equal success with pyrolysis oils. NO_x emissions should be controllable using staged combustion, low-NO_x burners, or other similar approaches.

In combustion systems such as this, where overall NO_x emissions are dominated by fuel nitrogen, the fuel nitrogen conversion efficiency is a convenient term to use in discussing trends. The conversion efficiency is the ratio of NO_x molecules in the effluent to fuel nitrogen atoms in the feed. The normalization to 3% O_2 is not required to determine this ratio. The fuel nitrogen conversion efficiency can exceed 100% if there is significant contribution to NO_x by thermal or some prompt mechanisms. In practice, conversion efficiencies for fuels containing significant nitrogen are in the range of 20-80 %.

CONCLUSIONS

NO_x measurements were completed for two pyrolysis oils produced by the same process but differing in fuel nitrogen content. Combustion tests were conducted in a

These data indicate: (1) fuel nitrogen conversion efficiency increases with increasing oxygen concentration if flame temperature is held constant, (2) fuel nitrogen conversion efficiencies decrease with increasing fuel nitrogen content (NO_x levels increase, but conversion efficiencies decrease), and (3) NO_x emissions are dominated by NO, which is primarily formed from fuel nitrogen.

Acknowledgements

This research was funded by the Department of Energy Office of Energy Efficiency and Renewable Energy through the National Renewable Energy Laboratory (NREL). The authors acknowledge the contributions of Donald Hardesty and Richard Bain as the Sandia and NREL Program Managers, respectively. The authors are also grateful to the assistance of Gian Sclippa (TADD Technical Services) and Howard Davis (Yale) in operating and maintaining the MFC and collecting data.

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Combustion Characterization Of Wood-Derived Flash Pyrolysis Oils In Industrial-Scale Turbulent Diffusion Flames

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ABSTRACT

An experimental investigation of two wood pyrolysis oils produced by the ENSYN and Waterloo flash pyrolysis processes was conducted in combustion tunnel of the MIT Combustion Research Facility. The purpose of the experiments was to compare the pollutant formation and combustion characteristics of these pyrolysis oils to those of No. 2 fuel oil, and to identify the special requirements for utilizing pyrolysis oils in practical systems.

Furnace exit and in-flame measurements of gas composition, soot concentration, and temperature were made using intrusive traversing probes in 1 MW turbulent diffusion flames with high swirl. A high speed camera was used in the near burner field to record combustion instability, as well as the atomization difficulties that were encountered when burning the pyrolysis oils. Several fuel filtration, heating, and atomization configurations were tested with the pyrolysis oils.

The experiments showed that the Ensyn pyrolysis oil flames performed comparably to No. 2 fuel oil, producing slightly higher NOx and CO emissions (108 vs 80 ppm NOx, and 35 vs 13 ppm CO @ 3% O2). The Ensyn oil required more frequent filter changes, but otherwise could be used with the same fuel delivery system and operating procedure as No. 2 fuel oil. Soot concentration did not differ measurably for the two fuel types.

INTRODUCTION

Recent advances in pyrolysis technology have made possible relatively economical methods for producing liquid fuels from a number of biomass feedstocks. With commercial production of these oils becoming increasingly likely in the near future, attention is now being focused on issues surrounding pyrolysis oil utilization and applicability to various industrial processes. The experimental study described below partly addresses this need by investigating the combustion characteristics and special handling requirements of two wood pyrolysis oils in a turbulent diffusion flame of a scale typical of those found in industrial burner applications. In particular, pollutant formation, combustion stability, and fuel handling characteristics of the two pyrolysis oils were compared to No. 2 petroleum fuel.

The pyrolysis oils were supplied by ENSYN Technologies, Inc. of Ottawa, Canada and Union Fenosa of Madrid, Spain. The properties of these fuels as well as those of the No. 2 petroleum fuel are listed in Table 1.

EXPERIMENTAL PROCEDURE AND APPARATUS

Measurements of gaseous and solid (soot) species concentration were made at the exit of the furnace and at various points in the flame. The behavior of the fuel in the feed lines and the fuel gun atomizer, and the combustion characteristics such as flame stability, combustion efficiency and pollutant emissions were determined for the effects of the fuel type, fuel pre-processing, type of atomization, and excess O2 in the stack. Video recordings of the flames were made through inspection doors located near the burner.

The experiments were performed at the MIT Combustion Research Facility using the Radially Stratified Flame Core Burner, an experimental low-NOx burner. The experimental furnace (Figure 1) is a refractory lined, water cooled 4.5 m x 1.2 m x 1.2 m combustion tunnel. It is of sectional design, the sections being partially or wholly cooled, permitting variable heat extraction along the axis of the flame and an accurate simulation of the temperature history in practical flames. An access door in each of the furnace sections allows detailed measurement of flame temperature and composition with intrusive traversing probes, including a suction pyrometer for temperature and water cooled suction probe for gas composition.

The firing rate was maintained at approximately 1.0 MW throughout the trials, corresponding to feed rates of 64 kg/h for the No. 2 distillate fuel and 163 kg/h for the biomass oils. The burner air flow rate was comparable for the three fuels, as shown in Table 1.

The oils were fed from a large container by use of a Moyno screw-type pump. The oils were filtered through 60 mesh screens at the pump exit and again at the end of the 15 m long steam/water jacketed fuel feed lines. The fuel then passed through a 230 micrometer filter at the fuel gun, where it was atomized by a steam-assisted 6-hole atomizer which is typically used for heavy fuel-oil. The biomass oils were heated to 60 °C and fed at 6 atm.

Difficulties with feeding the ENSYN oil were encountered when air-assisted atomization was used, resulting in frequent atomizer clogging. The 60 mesh filters located at the pump exit required changing for every 175 kg of oil filtered. By employing steam atomization and regular filter changes, the ENSYN oil could be combusted in stable and continuous manner.

There were a number of unsuccessful attempts to obtain a smooth feed of the Union Fenosa oil. The feed system was configured as with the ENSYN fuel, and then variations were attempted with oil temperature, air or steam atomization, fuel flow rate, and filter mesh size. In all cases the fuel was found to plug the atomizer tip and the fine filter, preventing continuous operation. Because of these difficulties, gas composition and temperature measurements with the Union Fenosa oil were not made.

It should be noted that the ENSYN oil was pre-filtered to 25 micrometers at the production plant prior to its delivery to MIT, whereas the Union Fenosa oil was delivered unfiltered. A small batch of the Union Fenosa oil was mixed with ethanol and it was found that at 15 vol % ethanol, the fuel feeding was no longer problematic and allowed stable combustion. At 7 vol %, the oil behaved as without the added alcohol.

RESULTS AND DISCUSSION

As shown in Figure 2, NO emission from the ENSYN oil was comparable to that of the No. 2 petroleum fuel for low levels of excess O2 (108 vs 80 ppm NO, respectively); however, as excess O2 increased, the NO emission from the bio-oil flame increased more rapidly than for the No. 2 flame. This is due to the higher fuel bound nitrogen (Fuel-N) input with the biomass fuel, particularly since the combined effects of higher mass concentration of fuel-N and the lower heating value results in a 5.4:1 ratio in the fuel-N inputs of the bio-oil and the No. 2 fuel oil.

The effect of excess O2 on CO emission is given in Figure 3. While the CO emission values are generally low for both fuels, it is clear that the CO concentration increases steeply in the bio-oil flame as the excess O2 is reduced to below 3%. The higher C/H ratio in the biofuel flame makes it more prone to both the emissions of CO and soot, as shown in Figure 4, where the soot

concentration at the flame axis is plotted as a function of axial distance from the burner face. The stronger soot forming tendency of the bio-oil flames reported in Figure 4 agrees qualitatively with the higher visually observed luminosity of the bio-oil flames. The solid particulates collected in the soot trap did not indicate a size difference which would trace to the original particulate in the bio-oil.

In order to better understand the combustion behavior of the ENSYN and No. 2 fuels, a detailed flame structure study was made in which in-flame gas composition and temperature were measured at many axial and radial positions in the near-burner flow field. For these experiments, the air flow rate was maintained at approximately 880 Nm^3/h, corresponding approximately to 3% excess air for the bio-oil when fired at 1.1 MW. The No. 2 fuel oil feed rate was reduced relative to that of the bio-oil to give the same exit O2 concentration, and about the same heat input.

The spatial distributions of temperature, CO, O2, HC, and NO concentrations are plotted in Figures 5 through 10. The contour plots show that the bio-oil flame has greater radial gradients in temperature and species concentrations, indicating that the fuel-jet penetrates further into the furnace before it mixes with the surrounding combustion air. This is due to the greater mass flow rate, and therefore linear momentum, of the bio-oil jet relative to the No. 2 fuel jet. As a result, the differences in species and temperature distributions between the two flames should not be attributed solely to intrinsic differences in the fuels. The detailed flame maps can be regarded as a representative comparison of the combustion behavior of the bio and petroleum fuels as would occur in cases where bio-oil is substituted for No. 2 oil in furnace applications while maintaining excess air and thermal input approximately constant.

The near burner region of the flame ($X/D < 3$) is of special interest for NO emission because the pyrolysis reactions in this region reduce NO and its precursors to N2. As shown in Figure 5, NO concentrations are high initially for the bio-fuel due to the conversion of Fuel-N in addition to the "prompt NO" formation at the flame front, but there is strong reduction of NO in the fuel-rich zone along the flame axis. Consistent with other fuel-nitrogen bearing flames, the region of most

intense NO destruction occurs where the light hydrocarbon concentration (shown as equivalent CH_4 in Figure 6) is highest, probably due to the NO "reburn" mechanism which relies on H, OH, and CH_i fragments to decompose NO to NH_i and N_2. In the No. 2 oil flame, the NO concentrations were lower than with the bio-oil flame, largely due to the absence of Fuel-N.

Interestingly, CO concentration (Figure 7) in the bio-oil flame decays more rapidly than in the No. 2 flame, though the CO concentration remains consistently higher at the furnace exit for the bio-oil cases. As expected, the peak temperatures (Figure 8) in the bio-oil flames were significantly lower (~ 100 K) than in the No. 2 cases, largely as a result of the lower heating value of the bio-oil.

Taken together, the detailed flame maps indicate no fundamental differences in the macro-scale combustion behavior of the wood pyrolysis oil and No. 2 petroleum fuel that would act as a barrier to utilizing the pyrolysis oil in industrial scale furnaces. Based on the experiences at the MIT CRF, it would seem that the difficulties associated with fuel delivery (atomization and filtration) are more critical, but not insurmountable.

Table I. Evaluation of Fuels

Fuel Description	No. 2 Fuel	ENSYN Tech.	Union Fenosa
Feedstock	N.A.	Hardwoods	Eucalyptus
Moisture(%)	0	19	23
HHV(dry,MJ/kg)	45	25	21
Specific Gravity	0.859	1.235	1.24
Viscosity	2.7(cSt,40 C)	1154(cSt,25 C)	579(cP,25 C)
Solids	0.05	0.65	0.94
Ash	0.05	0.04	0.12
Ultimate Analysis (wt%,daf)			
C	86.94	59.46	58.08
H	12.48	6.22	5.97
N	0.02	0.06	
S	0.3	0.016	0.1
O	0.17	34.26	35.68
Fuel Feed Rate(kg/h)	64.0	163.4	
Firing Rate(LHV,MW_{th})	1.07 MW	1.06 MW	C 0.9 MW
Stoichiometric Air(Nm^3/hk)	705	766	692
Burner Air Flow (Nm^3/h)	809	880	.794

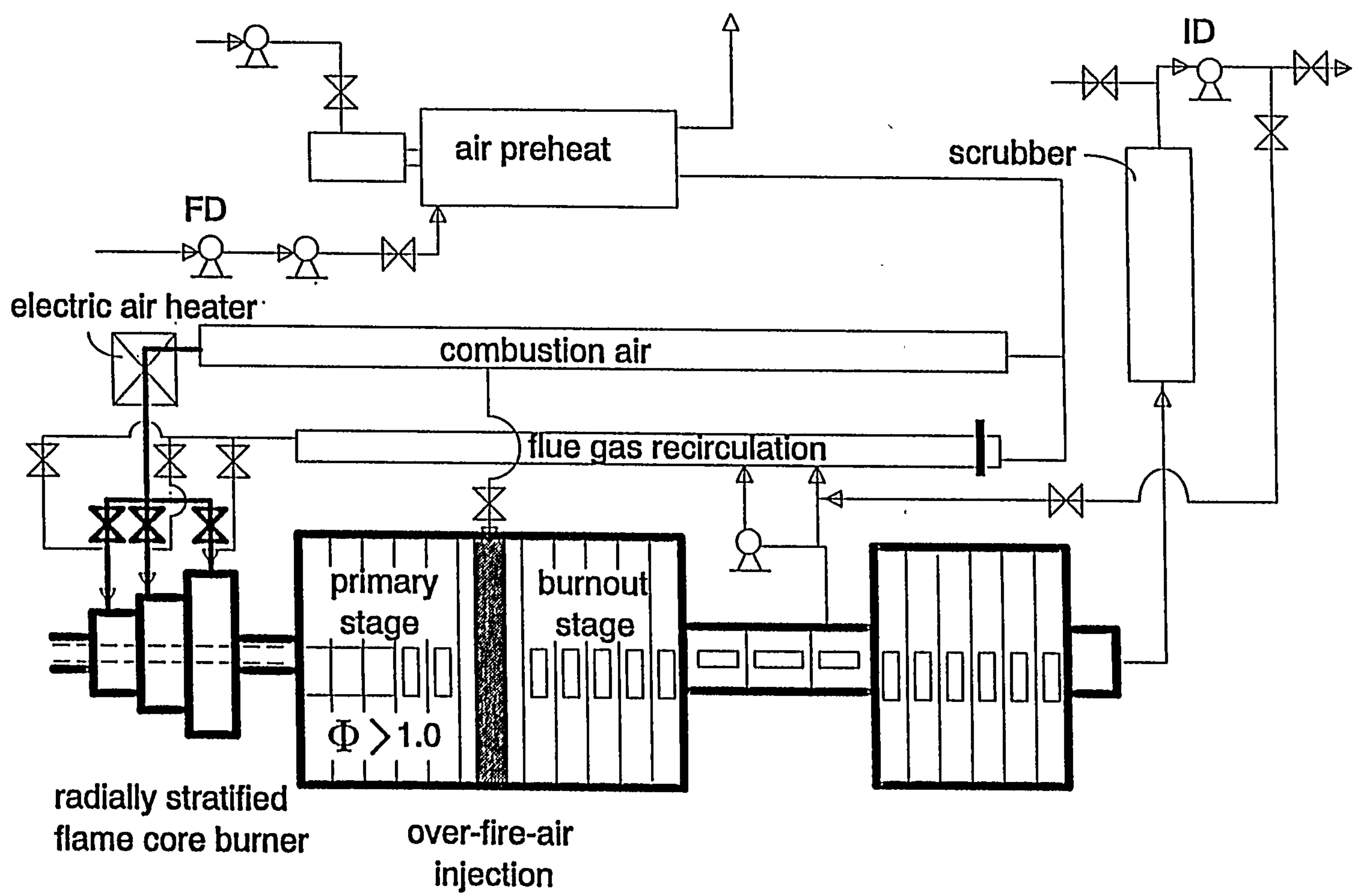


Figure 1. Schematic of the MIT Combustion Research Facility

Figure 2. Effect of Excess Oxygen on NO Emission

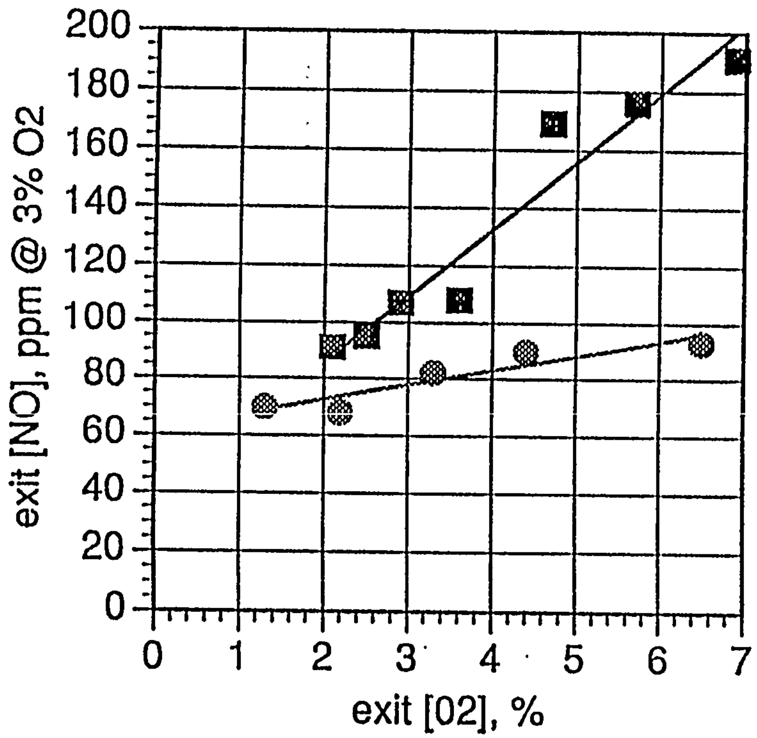
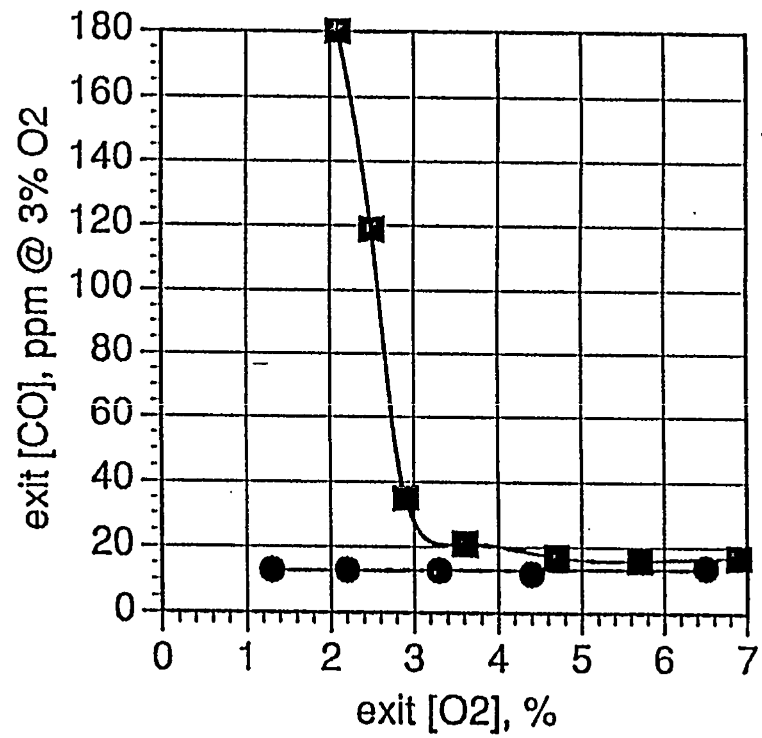


Figure 3. Effect of Excess Oxygen on CO Emission



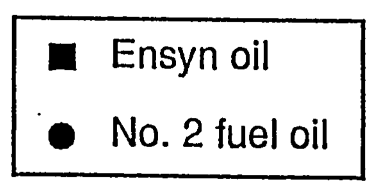
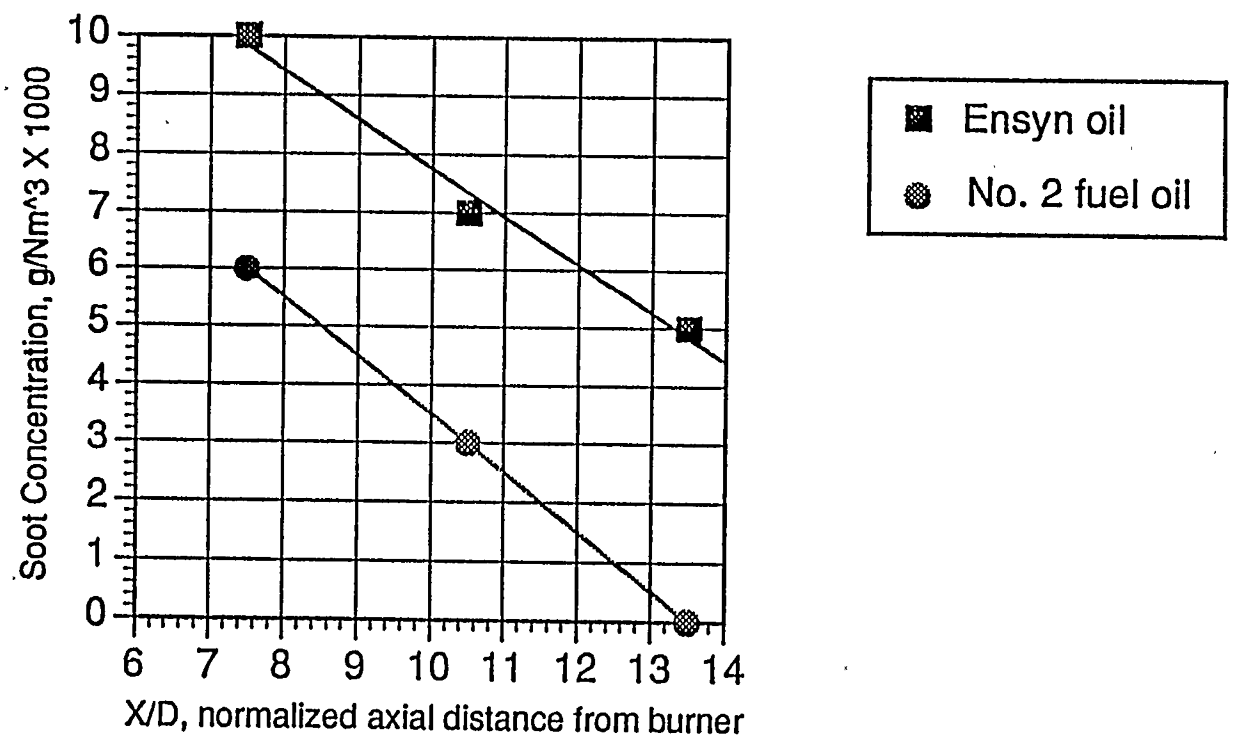


Figure 4. Centerline Soot Concentration (3% excess O2)



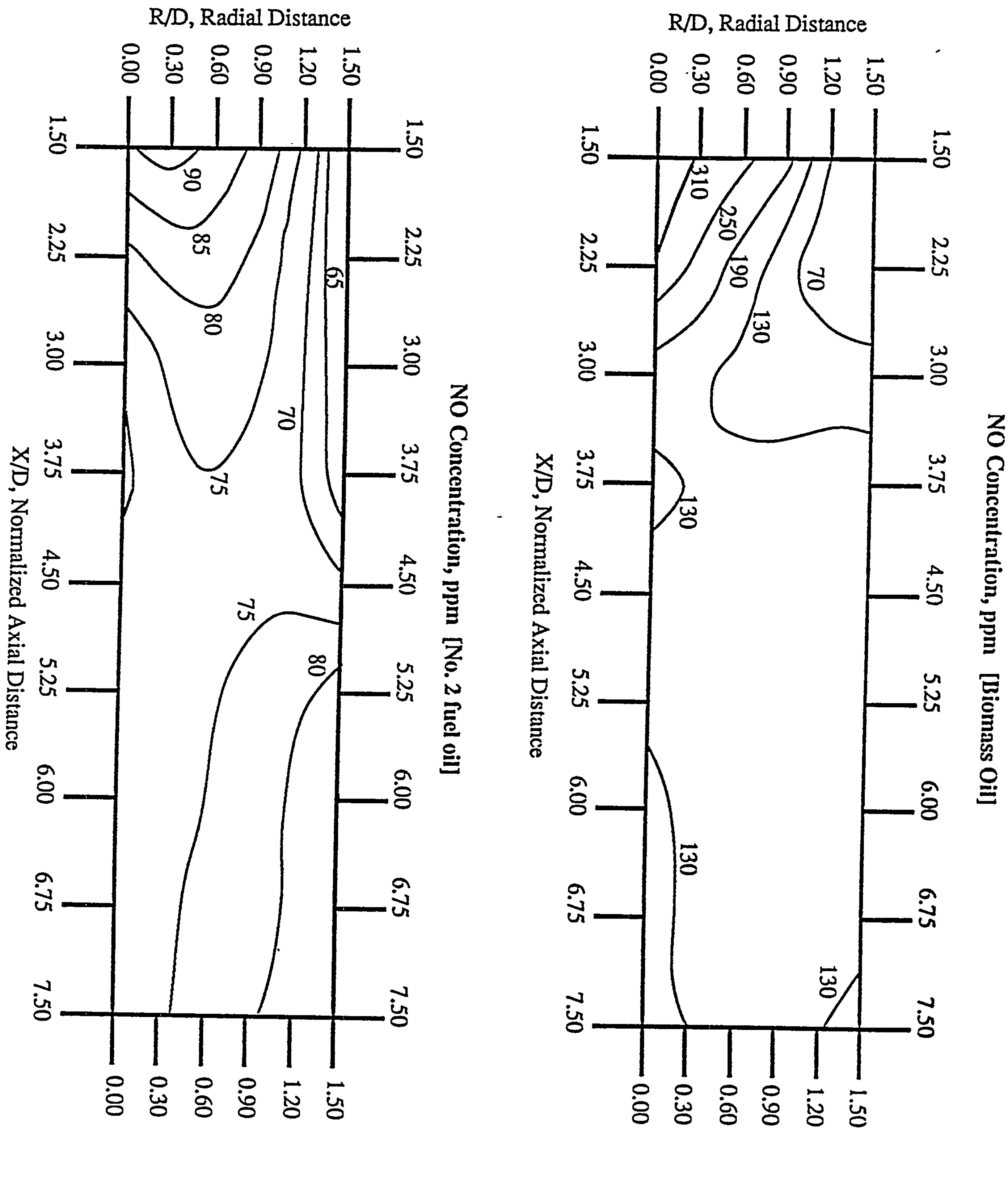


Figure 5. Measured In-Flame NO Concentration (D = 30 cm)

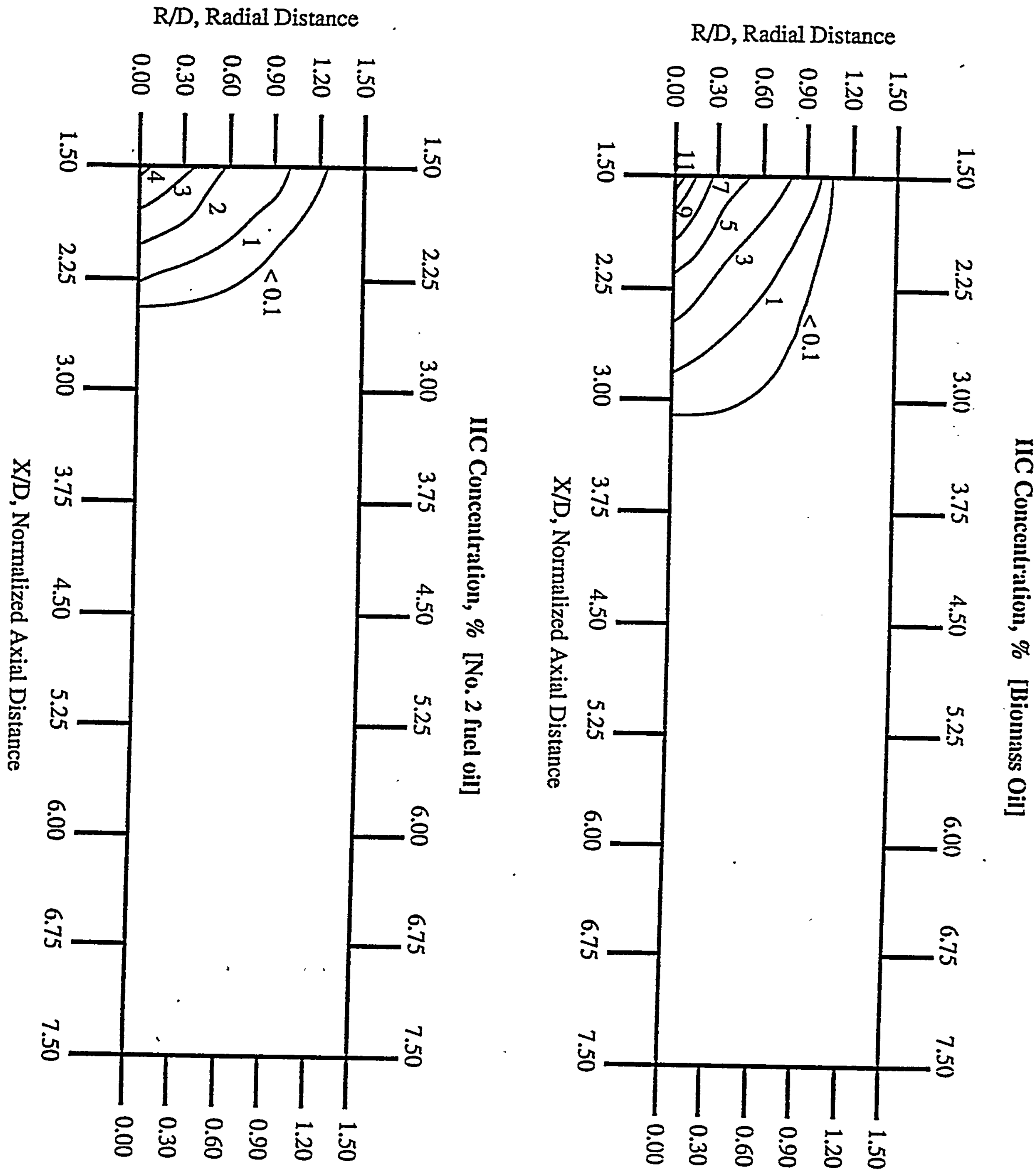


Figure 6. Measured HC Concentration

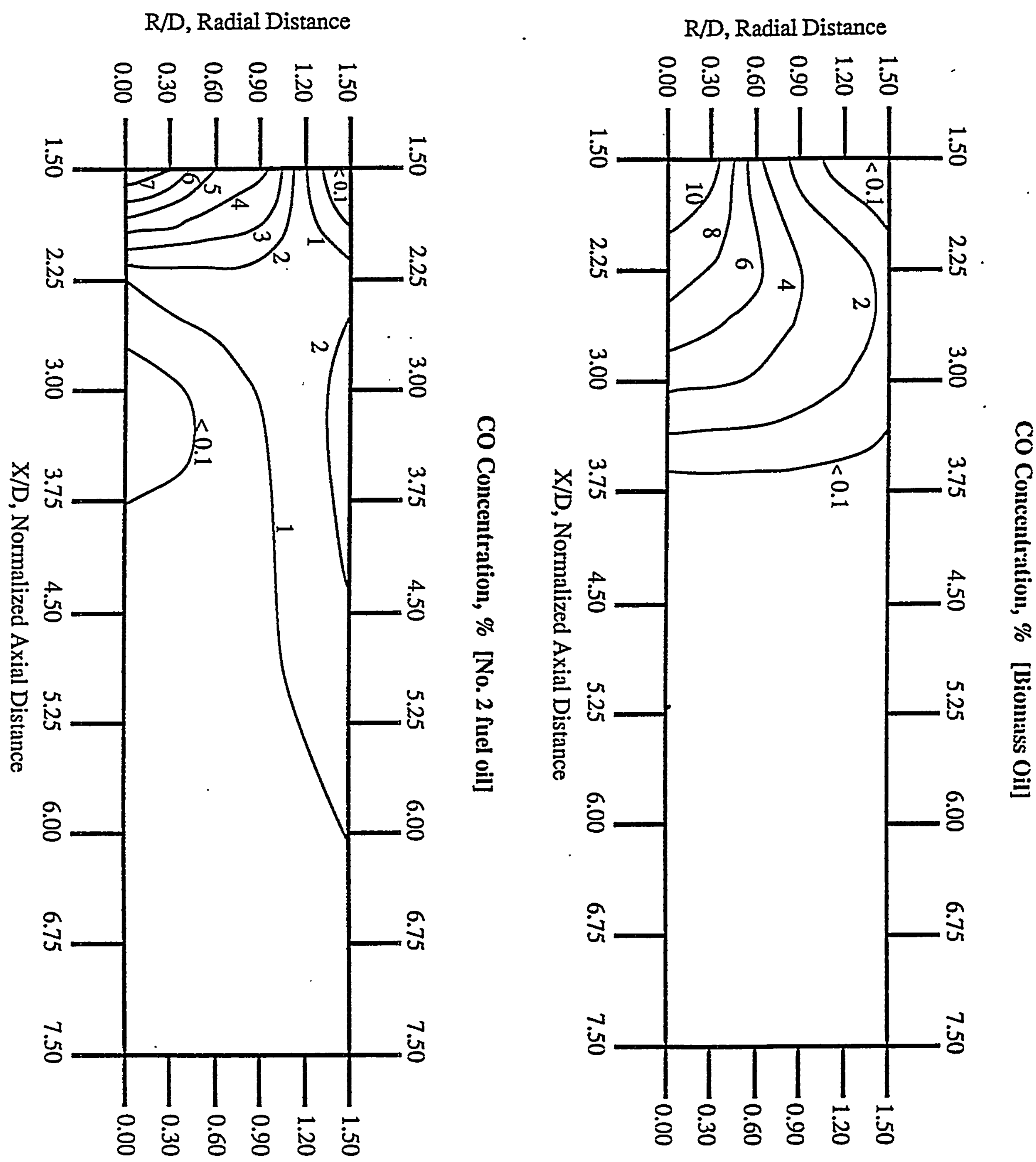


Figure 7. Measured CO Concentration

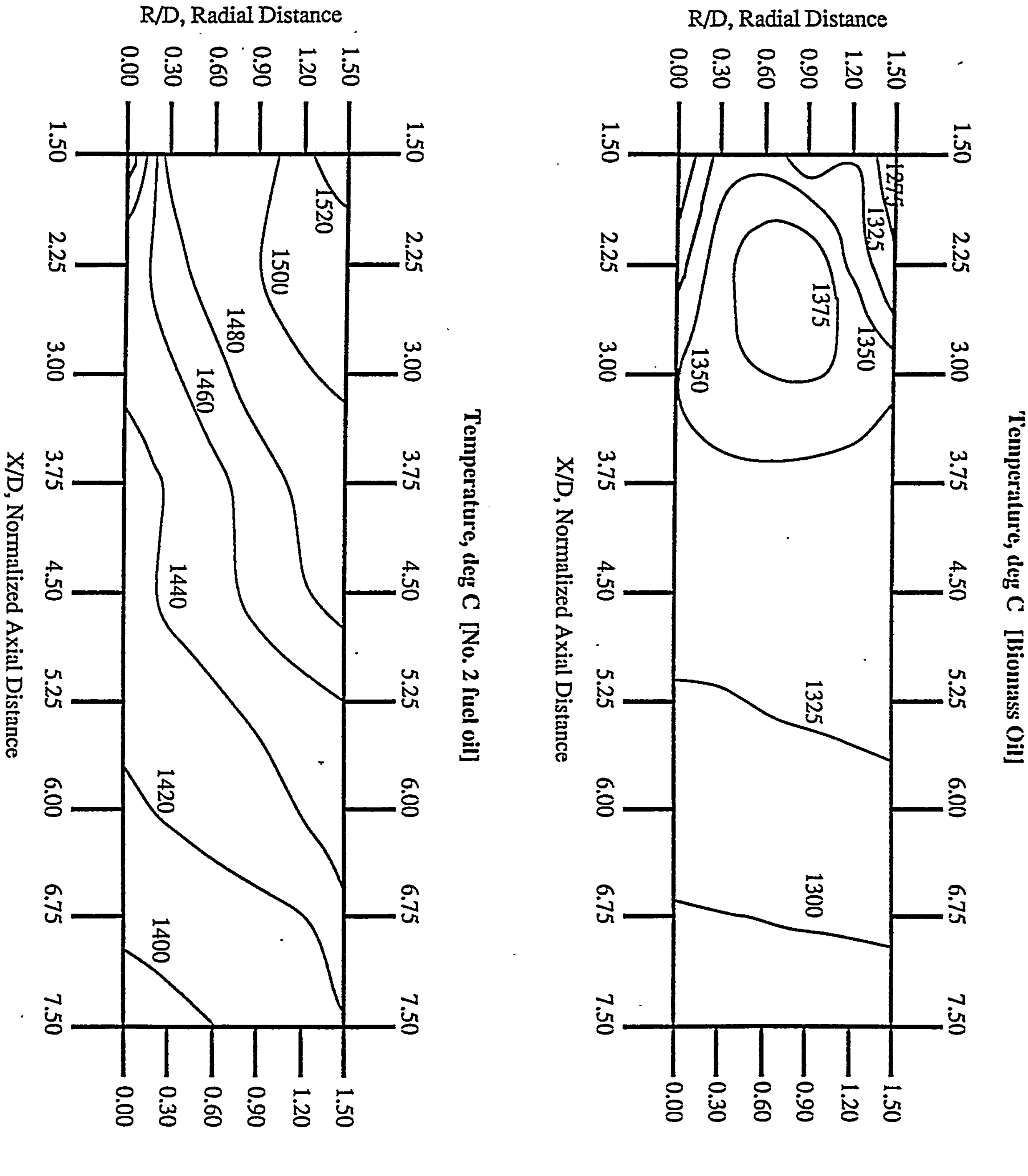


Figure 8. Measured Gas Temperature

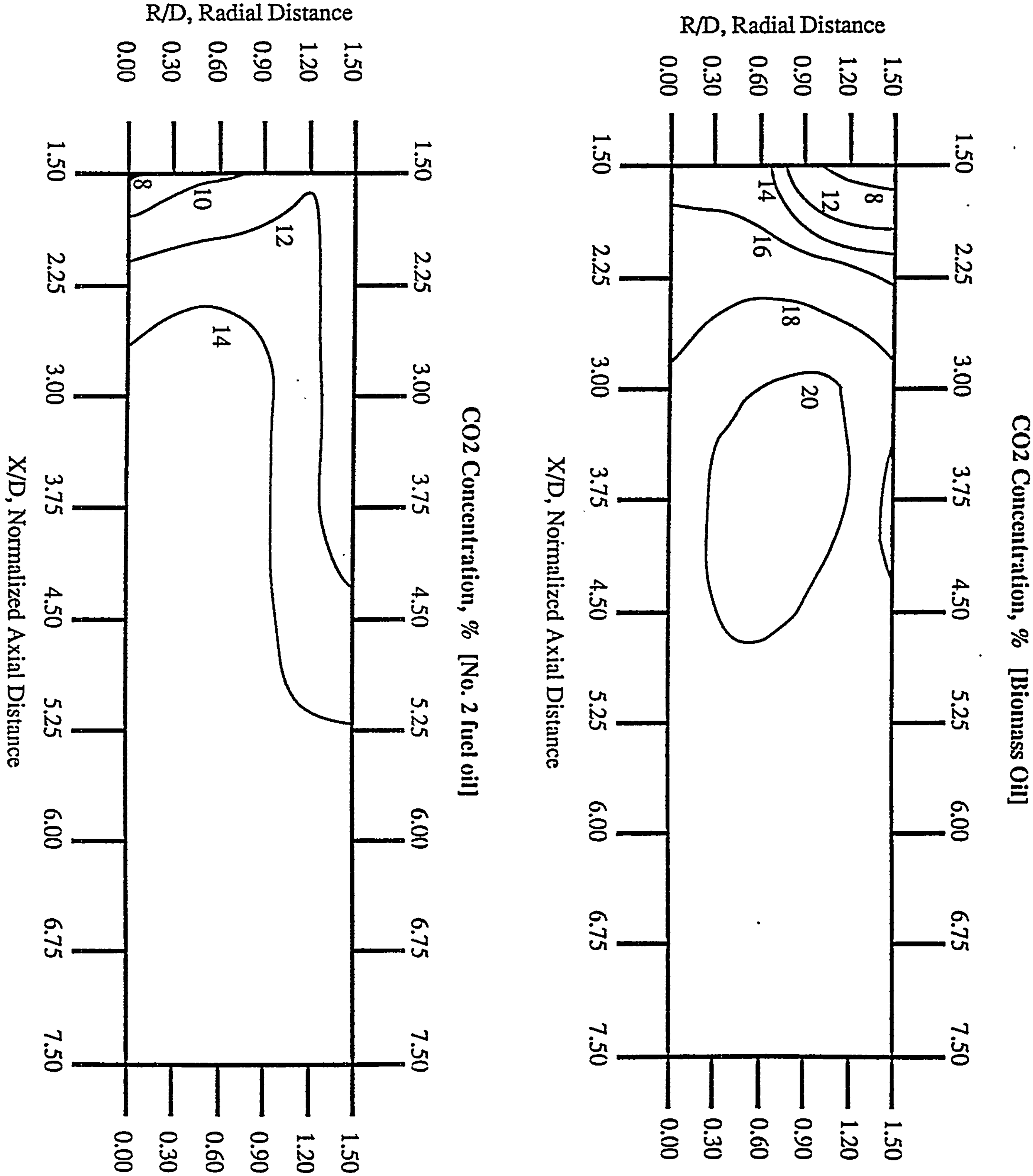


Figure 9. Measured CO2 Concentration

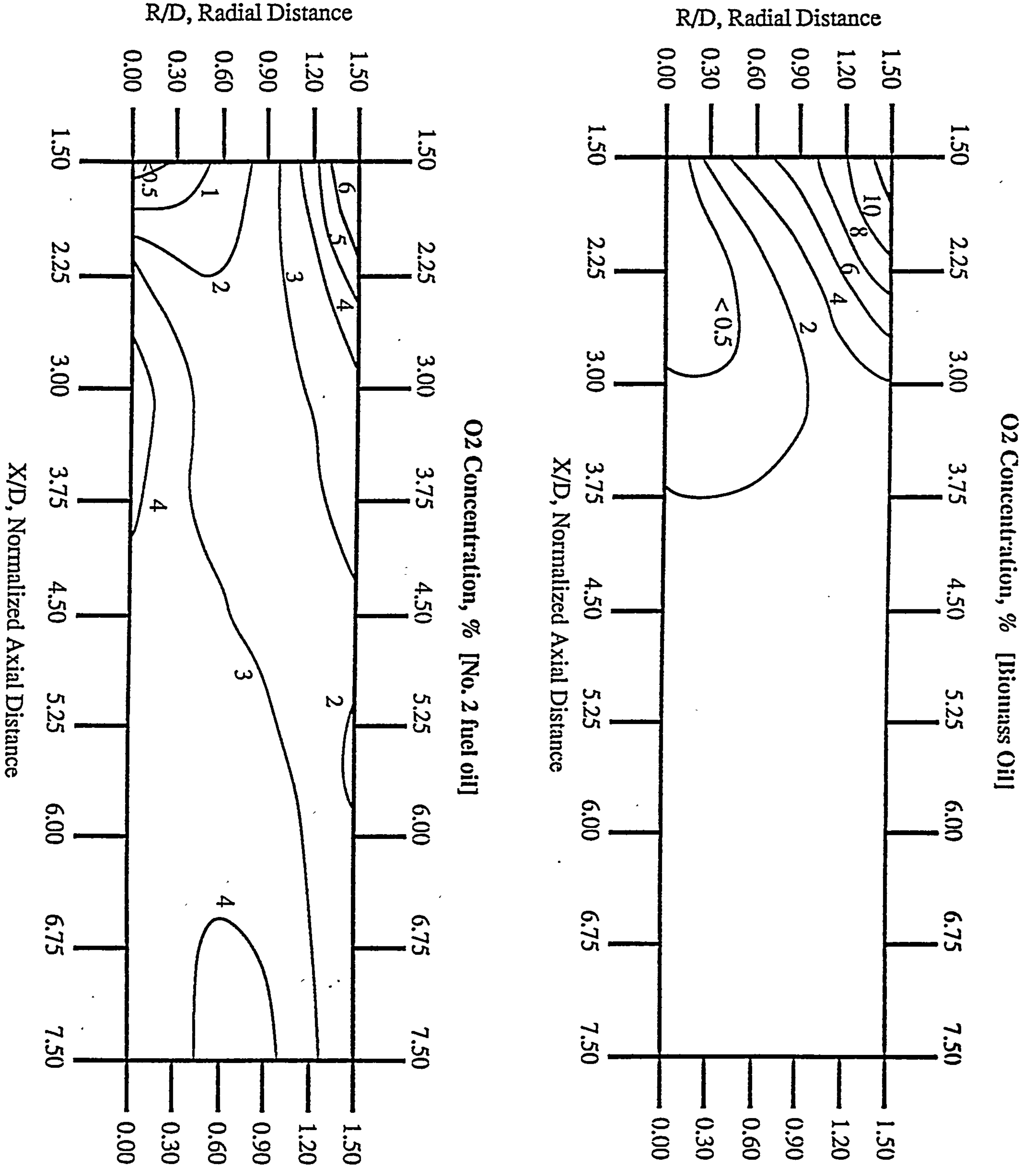


Figure 10. Measured O2 Concentration

ALKALI, CHLORINE, SO_x, AND NO_x RELEASE DURING COMBUSTION OF PYROLYSIS OILS AND CHARS

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Abstract

Hot gases liberated during the combustion of small pyrolysis oil and char samples in a variable temperature quartz tube reactor were directly sampled with a molecular beam mass spectrometer (MBMS) system, constructed and operated at the National Renewable Energy Laboratory. Four of the pyrolysis oils screened in this study (two switchgrass oils, an oak oil and a poplar oil) were produced in the NREL vortex reactor. The other three oils screened (a switchgrass oil, a poplar oil, and a corn stover oil) were produced in a laboratory scale (2 inch diameter) fluidized bed combustor. The biomass chars were recovered from the hot filters on the NREL vortex reactor during pyrolysis oil production. Alkali metal is sequestered in the char fines during the production of biomass-derived pyrolysis oils which suggests that efficient filtering should yield a lower alkali metal-containing pyrolysis oil. This result is desirable if pyrolysis oils are to become a competitive fuel for use in turbine combustors to generate power. The nitrogen, sulfur, and chlorine content of a given pyrolysis oil is a function of the starting feedstock material. High nitrogen, sulfur, and chlorine-containing biomass feedstocks yield pyrolysis oils with corresponding high levels of nitrogen, sulfur, and chlorine. NO_x and SO_x release have important environmental implications, and releasing chlorine can lead to increased corrosion in combustion facilities.

Introduction

Biomass-derived pyrolysis oils must contain very low levels of alkali to become competitive fuels for use in turbine combustors to generate power. Based on standards set for traditional petroleum fuel oils, turbine manufacturers require total alkali (Na and K) levels in the sub-ppm range.[1] Controlling releases of NO_x and SO_x during pyrolysis oil combustion must be considered to alleviate environmental concerns. Chlorine releases from pyrolysis oil combustion will have important implications concerning corrosion of heat transfer surfaces in boilers and turbine blades in direct pyrolysis-oil-fired facilities. The transformation of nitrogen, sulfur, and chlorine during the production of biomass-derived pyrolysis oils has not been studied in detail. When pyrolysis oil is produced, the majority of the alkali metal present in the starting biomass material remains sequestered in the char fines. The alkali metal content of the oils, therefore, is thought to be predominantly a function of the amount of char fines suspended in the oil. The combustion of biomass-derived oils and chars was studied to investigate the fate of nitrogen, sulfur, and chlorine and alkali metal sequestered in the char and oil during the production of pyrolysis oil from biomass.

Experimental Approach

The release of alkali vapor species, NO_x, SO_x, and chlorine during the combustion of selected biomass-derived pyrolysis oils and chars was monitored and studied using a direct sampling, molecular beam mass spectrometer (MBMS) system constructed and operated at the National Renewable Energy Laboratory. The MBMS system is ideally suited for studying the high

temperature, ambient pressure environments encountered during the present screening studies. The integrity of the sampled, high temperature combustion gases is preserved by the free-jet expansion which effectively quenches chemical reactions and inhibits condensation. As a result, reactive and condensable species remain in the gas phase at temperatures far below their condensation point for long periods of time in comparison to reaction rates. This apparatus(2,3) and using the MBMS to study alkali metal transport and speciation during biomass combustion(4,5) has been described in detail in the literature so only a brief discussion is presented below.

Oil and Char Samples

Seven different oils were investigated during the present study. Four of the oils were produced in the NREL vortex reactor:(6) switchgrass oil (high alkali, run #146A); oak oil (run #154); switchgrass oil (low alkali, run #157); and poplar oil (run #160). During the production of the first two oils (run #146A and run #154), the char fines were filtered out of the hot gas stream using a cyclone. A hot baghouse filter was used to remove particulates during the production of the second two oils (run #157 and run #160). The remaining three oils were produced in a laboratory scale (2" diameter) fluidized bed combustor (FBC).(7) These oils were produced from switchgrass (time 0, run #101), poplar (time 0, run #4), and corn stover (time 0, run #2), respectively. The major physical difference between the oils produced in the two reactors is that the oils produced in the vortex reactor were considerably less viscous than the fluidized bed reactor oils. This difference is most likely because of longer residence times in the vortex reactor which leads to increased thermal cracking. The char samples investigated in this study(8) were collected from the chars remaining after biomass was pyrolized in the NREL vortex reactor. The following char samples were received: oak char (run #154); poplar char (run #156); and switchgrass char (run #157).

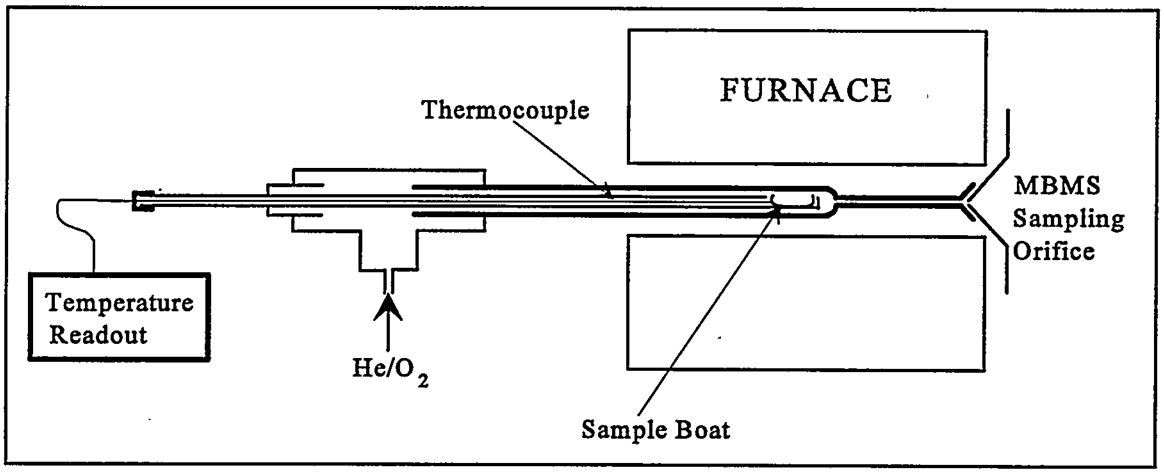

Figure 1. A schematic of the quartz tube reactor used to study biomass-derived pyrolysis oil and char combustion.

Molecular Beam Mass Spectrometer/Quartz Tube Reactor Apparatus

Ten to fifty milligrams of each sample was loaded into hemi-capsular quartz boats which were then placed in a platinum mesh basket attached to the end of a quarter-inch diameter quartz rod. This quartz rod was then inserted and translated into the heated zone of a quartz tube reactor enclosed in a two-zone variable temperature furnace as illustrated in Figure 1. The experiments simulate the continuous combustion of the sample from initial heating to ignition to complete char burnout and ash "cooking." Furnace temperatures during these screening studies were maintained at 1100°C and 800°C, respectively. Gas temperatures near the quartz boat were measured with a type K thermocouple inserted through the quartz rod. The actual boat temperature and the flame temperature

of the combustion event were not measured. The atmosphere in the reactor consisted of a flowing mixture of 20% oxygen in helium at a total flow rate of 4.4 standard liters per minute.

The molecular beam sampling system consists of a three-stage, differentially pumped vacuum chamber. A conical, stainless steel molecular beam sampling orifice is positioned at the downstream end of the quartz tube reactor to sample the high temperature, ambient pressure combustion gases. The tip of the sampling orifice protrudes into the furnace keeping it at an elevated temperature (not measured) to prevent alkalis and other species from condensing on the orifice. Sampled gases underwent a free jet expansion into the first stage of the vacuum system. A molecular beam was formed by collimating the gas stream with a conical skimmer located at the entrance to the second stage of the vacuum system. The molecular beam was directed into the ionization region of the mass spectrometer located in the third stage of the vacuum system. Electron impact ionization of the species in the molecular beam yielded ions that were filtered by a triple quadrupole mass analyzer and detected with an off-axis electron multiplier.

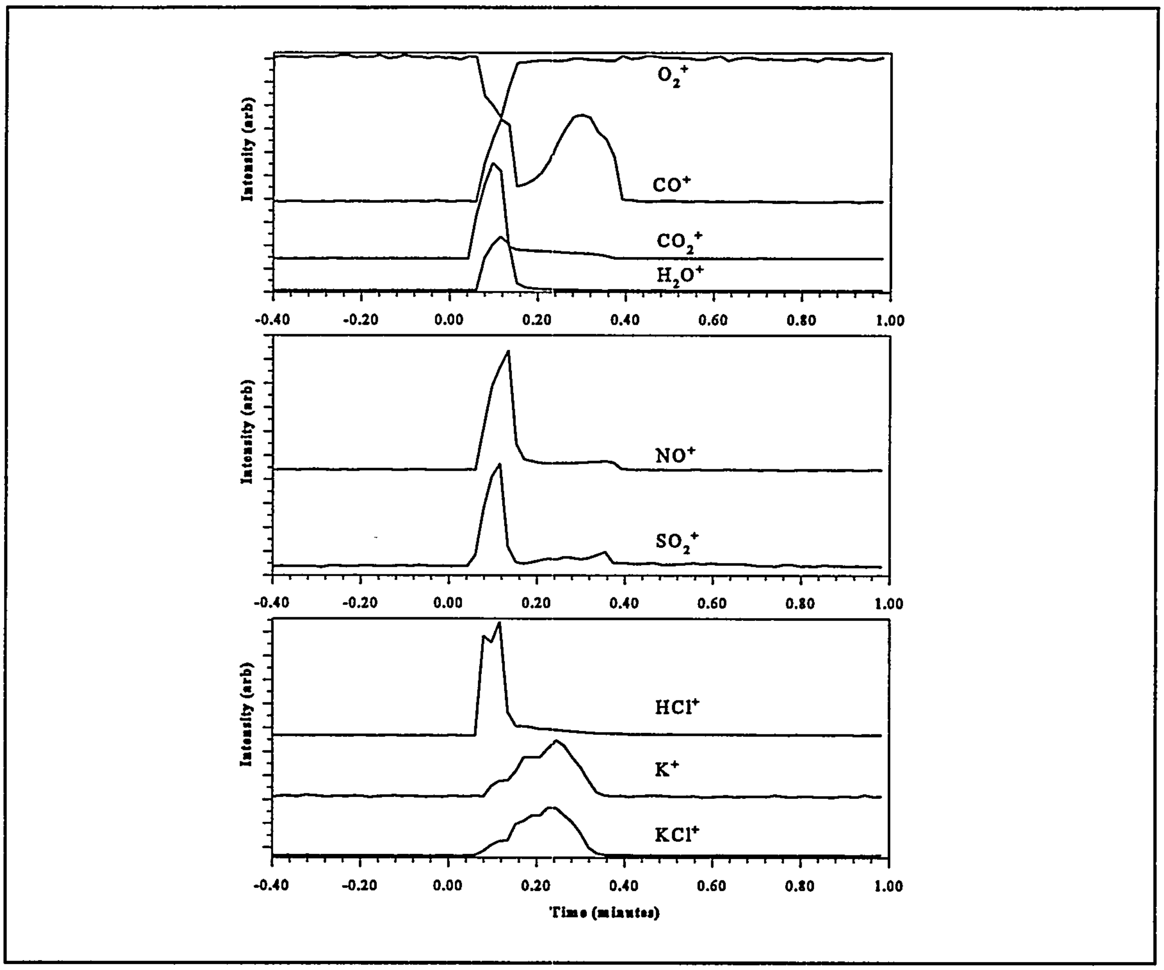

Figure 2. Time vs. intensity profiles of selected ions monitored during switchgrass combustion at 1100°C in 20% O_2 in helium. Relative ion intensities should not be compared.

As discussed in a previous report, biomass combustion occurs in three distinct phases.[4] For example, depicted in Figure 2 are the intensity versus time profiles for selected ions of interest

monitored during the combustion of switchgrass (*Panicum vergatum L.*) at 1100°C in 20% O_2 in helium. The relative intensities of different ions in Figure 2 have not been normalized, and therefore should not be compared. Following a period of time during which background spectra were collected, the sample was inserted into the high temperature zone of the reactor at time zero in Figure 2. Combustion was initiated very rapidly once the sample was inserted. The first phase, called the combustion or devolatilization phase, is dominated by the production of CO, CO_2, and H_2O while O_2 is consumed. A substantial fraction of the SO_2, NO, and HCl is also liberated during the combustion phase. After the volatile species have been completely liberated the char combustion phase begins. Most of the alkali metal containing vapors were released during the char combustion phase. Potassium chloride is the dominant alkali metal containing species released during switchgrass combustion. The final phase of the combustion process is termed the "ash cooking" phase. Most of the volatile matter has been liberated by the beginning of this phase, however, the remaining ash is left in the high temperature reactor to insure that all of the volatile matter has been released. The ash content of the pyrolysis oils studied is very low (less than 0.1% by weight). The biomass chars studied, however, can be as much as 10% ash. The switchgrass char is actually 22% ash by weight. In entrained combustion, the "ash cooking" phase will be limited to, at most, a few seconds, however, it could be much longer in a moving or fluidized bed combustor.

Combustion of Biomass Chars

The combustion behavior of the biomass chars is different compared to combustion of the biomass precursor. Depending on how completely the biomass was pyrolyzed, some volatile matter can be left in the char, and as a result, three separate phases of combustion were observed as in biomass combustion. In the following discussion, only the first two phases will be discussed. The majority of the volatile material has been released by the third or "ash cooking" phase during biomass char combustion.

As a distinction, phase 1 follows the acquisition of the background spectra, followed by phase 2, and the ash cooking phase. These phases are represented in Figure 3, which shows the temporal profile of the total ion current intensity recorded during switchgrass char (run #157) combustion in He/O_2(20%) at 1100°C. The sample is introduced into the high temperature region of the furnace at approximately 0.5 minutes in the figure. The initial peak in the total ion intensity corresponds to phase 1 and the average mass spectrum over this phase is presented in Figure 4. The switchgrass starting material was screened in the initial alkali screening studies[4] and is known to have a high alkali metal and chlorine content. Therefore, the corresponding switchgrass char is also expected to have a high alkali metal and chlorine content.

The ultimate analysis results of the switchgrass char, which are listed in the inset in Figure 4, confirm the high alkali metal and chlorine content. Compared to the parent switchgrass material, which is 0.83% K by weight (dry basis), the switchgrass char is 4.2% K by weight (dry basis). This clearly indicates that potassium was concentrated in the char when switchgrass was pyrolyzed. The mass spectrum averaged over phase 1 shown in Figure 4 indicates that this phase is dominated by the release of CO_2, CO, HCl, KCl, NaCl, and SO_2. Based on the measured intensities of the $NaCl^+$, KCl^+, and K_2Cl^+ (the KCl dimer fragment ion) signals indicated in Figure 4, a large fraction of alkali metal vapor was released during this phase of the switchgrass char combustion. The average mass spectrum over phase 2 of switchgrass char combustion is presented in Figure 5.

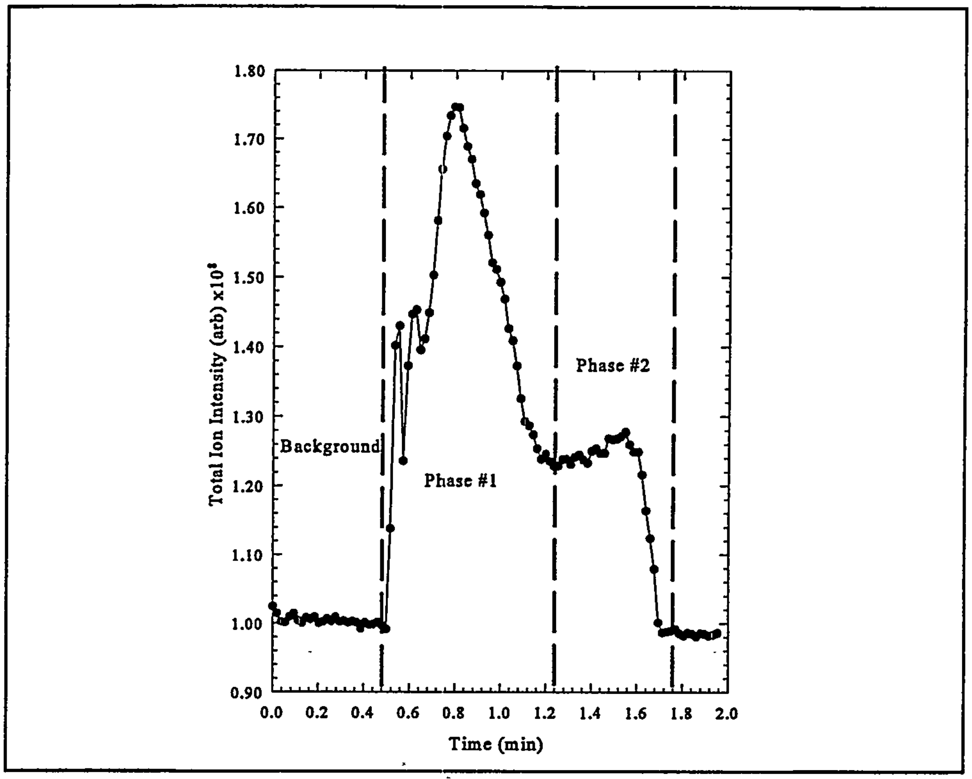

Figure 3. Temporal profile of the total ion current measured during switchgrass char combustion at 1100°C in 20% O_2 in helium.

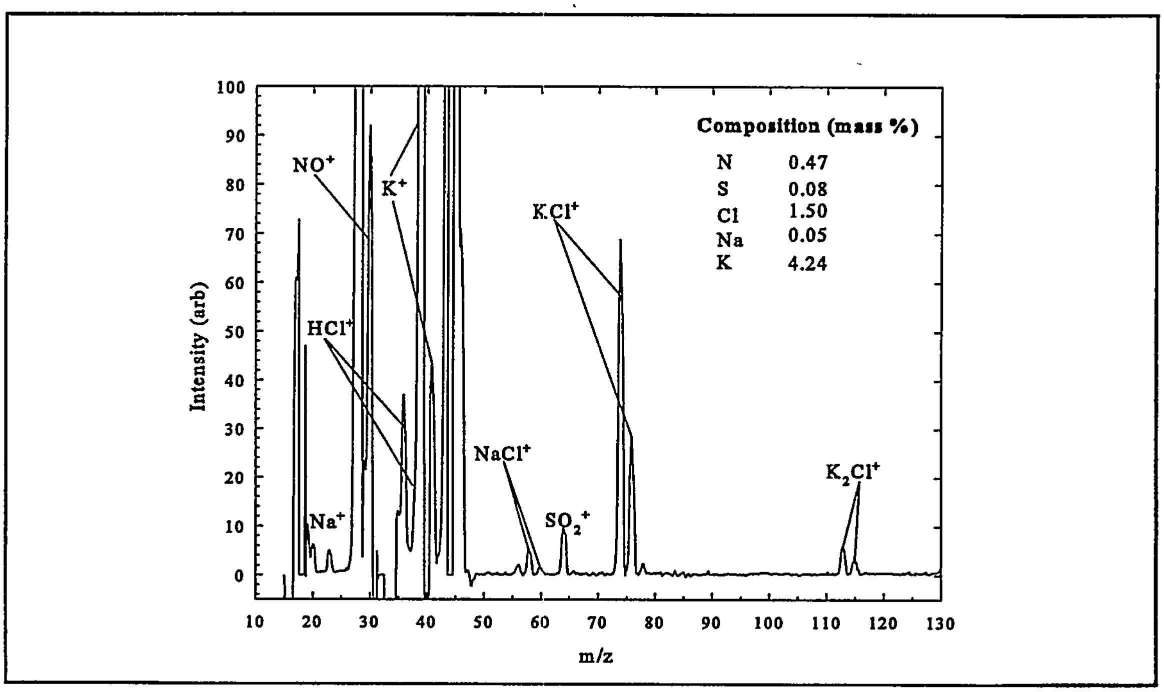

Figure 4. Average mass spectrum recorded during phase 1 of switchgrass char combustion at 1100°C in 20% O_2 in helium. Mass spectral intensity has been normalized to the background $^{34}O_2^+$ signal. Sample composition (dry basis) as determined in the ultimate analysis is listed in the inset.

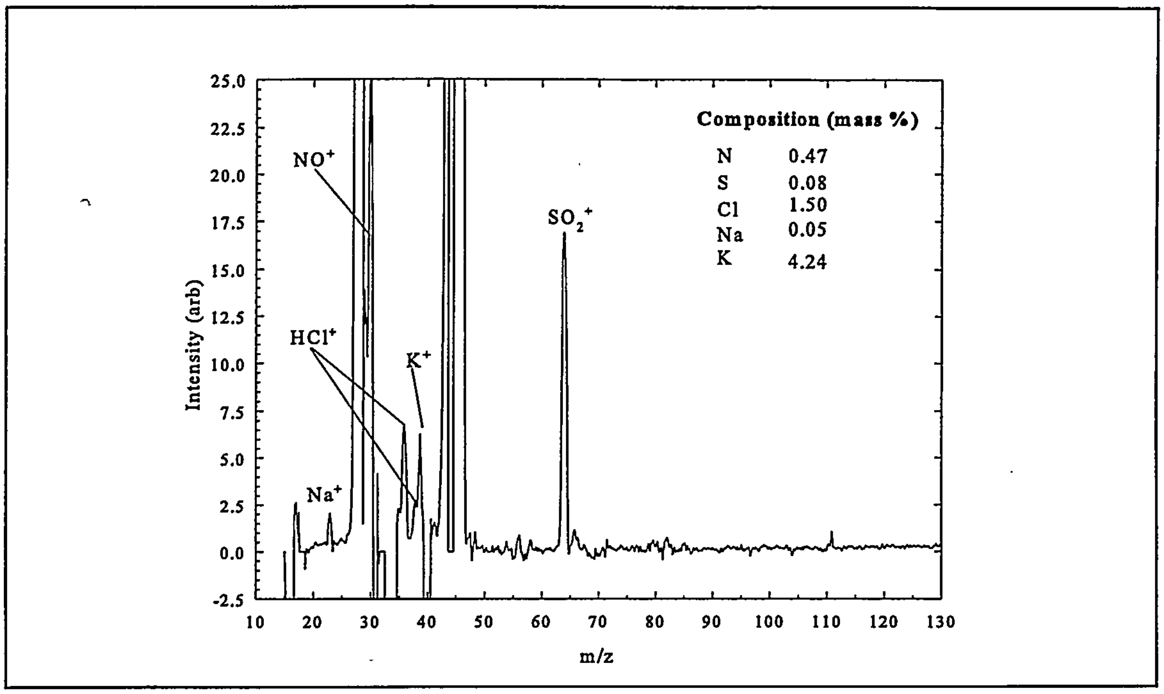

Figure 5. Average mass spectrum recorded during phase 2 of switchgrass char combustion at 1100°C in 20% O_2 in helium. Mass spectral intensity has been normalized to the background $^{34}O_2^+$ signal. Sample composition (dry basis) as determined in the ultimate analysis is listed in the inset.

In contrast to phase 1, the phase 2 mass spectrum indicates that little alkali metal vapor was released during this phase. This is substantiated by the absence of the KCl^+ and K_2Cl^+ peaks and only a small K^+ intensity at 39 amu. NO^+ and SO_2^+ are still observed in the phase 2 mass spectrum. These results indicate that alkali metal release during the combustion of switchgrass char occurs primarily in the form of the chloride in the first phase and possibly is shifted to the sulfate in the second phase.[4]

Oak and poplar are considered woody feedstocks which have relatively low levels of alkali metal. Consequently, the chars remaining after pyrolysis of oak and poplar are also expected to have low alkali levels. This is confirmed by the mass spectra averaged over the two phases during combustion of oak char (spectra not shown). Except for a small peak at 39 amu, assigned to K^+, no alkali metal containing species were identified in phase 1 of the oak char combustion. SO_2^+ and NO^+ in addition to the expected combustion products CO_2, CO, and H_2O were also observed during phase 1 of oak char combustion. The mass spectrum averaged over phase 2 of oak char combustion is very similar to the phase 1 spectrum. The most notable difference is the lack of NO released during phase 2. Apparently all of the nitrogen bound in the oak char is released during phase 1 of combustion.

The mass spectrum averaged over phase 1 during poplar char combustion confirms the low alkali metal content of the poplar char. Alkali metal vapor release was noted by the detection of K^+ at 39 amu and weak signals at 74 and 76 amu corresponding to KCl^+. NO^+ and SO_2^+ were also detected. These same species were detected during the char combustion phase of the precursor poplar combustion reported in the initial alkali screening studies.[4] Comparing the K^+ signals in the phase 1 mass spectra for oak char and poplar char combustion, it appears that twice as much potassium was released during poplar char combustion. Unlike oak char combustion, NO is released during phase 2 of poplar char combustion. Bound nitrogen was released throughout the combustion of poplar char.

The effect of temperature on the combustion of the biomass chars was investigated by screening the three chars discussed above at 800° C in He/O_2(20%). The duration of char burnout is about a factor of two longer at the lower furnace temperature. The main effect that temperature has on the combustion of the woody feedstock derived chars is the absence of the SO_2^+ peak at 64 amu. For the oak char, this also correlates with an absence of K^+ at 39 amu. This strengthens the argument that the primary alkali release for woody feedstocks is through vaporization and/or decomposition of potassium sulfate.[4] KCl^+ at 74 and 76 amu and the corresponding K^+ fragment ion at 39 amu can be identified in the mass spectrum recorded during phase 2 of poplar char combustion at 800° C. In the case of the switchgrass char, the majority of the alkali chloride release is now shifted to the second phase during combustion. This suggests that the mechanism of alkali metal release during the switchgrass char combustion is highly temperature dependent and may be because of the vaporization temperature of KCl.

Combustion of Biomass-Derived Pyrolysis Oils

The general combustion behavior of the oils is considerably different compared to combustion of solid biomass and chars. When the oil samples are inserted into the hot region of the reactor, the combustion produces a very luminous flame which is visible from the rear of the reactor. In contrast, a flame was not observed during combustion of solid biomass or char. The pyrolysis oil combustion event also appears more violent than that of solid biomass. As a result, a serious problem with PIN (Particulate Induced Noise) was encountered. Particulates (char-ash particles and/or aerosols) released during combustion become entrained in the gas flow and collide with metal surfaces inside the mass spectrometer. These collisions randomly produce ions that are detected. This results in a time-dependent, mass-independent signal that saturates the detector and obscures any mass spectral data recorded during the PIN event.

The PIN problem made screening the pyrolysis oils more difficult compared to previous studies with solid biomass material. We increased the residence time of the combustion gases (and particles) in the reactor to almost one second (compared to about 0.1 seconds for the solid biomass combustion) which reduced the PIN problem by allowing sufficient time for particle burnout. PIN continues to be a problem in monitoring pyrolysis oil combustion, however, the nature of pyrolysis oil combustion and the gases released can still be investigated.

Several observations can be made about the combustion of biomass pyrolysis oils upon analysis of the mass spectral data. As seen in Figure 6, which shows the total ion current profile versus time for FBC switchgrass oil at 1100° C in 20% O_2 in helium, the duration of the pyrolysis oil combustion is considerably shorter than combustion of solid biomass, and there is little indication of a char combustion phase during pyrolysis oil combustion. All of the parent feedstocks from which these oils have been produced have been screened for alkali release in the past.[4] As a result, the relative amounts of alkali metal, nitrogen, sulfur and chlorine present in the feedstocks is known. The screening studies of biomass chars discussed above also indicated that most of the alkali metal in the parent material is sequestered in the char leaving relatively low levels of alkali metal in the oils. The preliminary screening of these seven pyrolysis oils indicates that, indeed, the oils are low in alkali metal compared to the biomass precursors. As an example, Figure 7 displays the mass spectrum averaged over phase 1 during FBC switchgrass oil combustion. Similar to combustion of the solid feedstocks, it is easy to identify the major combustion products H_2O, CO, and CO_2 in the mass spectra recorded during the combustion of the pyrolysis oils. It is also possible to identify NO and SO_2 released during combustion of the pyrolysis oils. Individual alkali metal containing species were not detected, however, it is possible to identify the K^+ fragment ion from potassium containing species.

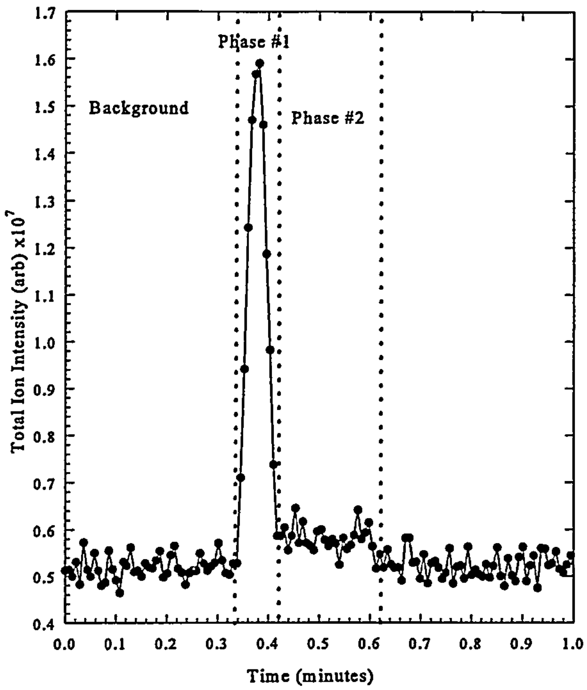

Figure 6. Temporal profile of the total ion current measured during FBC switchgrass oil (time 0) combustion at 1100° C in 20% O_2 in helium.

The mass spectra averaged during the combustion of the pyrolysis oils produced from biomass with a high chlorine content (switchgrass and corn stover) indicate a substantial amount of HCl was released. Most HCl was released during combustion of the FBC switchgrass oil. The parent feedstock has a high chlorine content which explains the HCl released during combustion of the oil. In general, the oils produced from switchgrass in the vortex reactor have lower chlorine content, in terms of HCl released during combustion, than the switchgrass oil produced in the fluidized bed combustor. In fact, no HCl is detected during combustion of the vortex switchgrass oil (run #157), which was produced using the baghouse hot gas filter to remove the particulate matter. Corn stover also contains high levels of chlorine which translates into large HCl signals in the mass spectra recorded during combustion of the corn stover-derived oil.

The amount of NO detected during combustion of the pyrolysis oils is relatively constant. Most NO is detected during combustion of the FBC corn stover oil. Corn stover has the most fuel-bound nitrogen (according to the ultimate analyses) of the four feedstocks used to produce the oils. In addition, the corn stover oil has the highest nitrogen content according to the ultimate analyses of the oils. The least NO (four times less) detected is during combustion of the vortex oak oil (run #154). The NO released during combustion of the switchgrass-derived oils is relatively consistent and does not appear to be a function of the way the oils were produced.

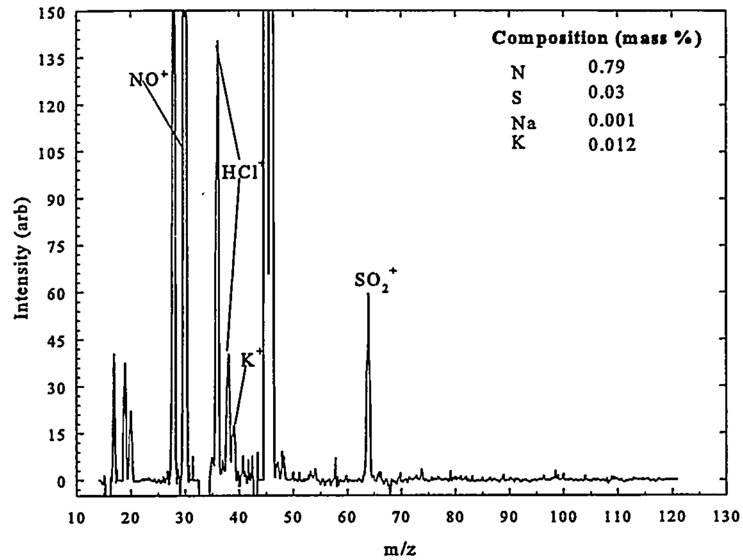

Figure 7. Average mass spectrum recorded during phase 1 of FBC switchgrass oil combustion at 1100° C in 20% O_2 in helium. Mass spectral intensity has been normalized to the background $^{34}O_2^+$ signal. Sample composition (dry basis) as determined in the ultimate analysis is listed in the inset.

Reducing the furnace temperature to 800° C has little effect on the combustion behavior of the seven pyrolysis oils screened in this study. The mass spectra averaged during the combustion of the poplar oils (produced in the FBC and vortex reactors, respectively) at 800° C are almost identical to the higher temperature results. Little change is also observed in the mass spectra averaged during the combustion of the vortex oak (run #154) and vortex switchgrass (run #157) oils compared to the higher temperature results (spectra not shown). The mass spectra averaged during combustion of the FBC switchgrass and corn stover oils and the high alkali, vortex switchgrass oil (run #146A) at the lower furnace temperature suggest that less SO_2 and HCl are released compared to the higher temperature results. The ratio of the SO_2 to HCl signals, however, is not a function of temperature indicating that the differences in the signal intensities may be just an artifact of scaling or differences in instrument response. Individual alkali metal containing species are still not observed during combustion of these oils at a lower furnace temperature.

Quantification of the KCl Released During Combustion of Switchgrass, Switchgrass Oil, and Switchgrass Char

The amount of potassium chloride, the dominant alkali metal containing species, released during the combustion of switchgrass char was quantified and compared to the amount of potassium chloride released during combustion of the parent feedstock. The amount of gas phase KCl released during combustion of switchgrass char at 1100° C and 800° C in He/O_2(20%) was quantified by a previously described procedure.[4] KCl standards were prepared by drying 100 µl of a 4.654 mM aqueous KCl solution in a quartz boat in air. This resulted in 35µg of solid KCl in the sample boat. Standards are inserted into the furnace in the same fashion as the biomass samples with the underlying assumption that all of the KCl is volatilized, and that the KCl/reactor wall interactions are identical for the standards, the biomass, and char samples. The area under the m/z=74 time profile was used to

quantify the amount of gas phase KCl liberated during switchgrass and switchgrass char combustion. This insures that the KCl released during all phases of combustion was taken into account. The results for the amount of KCl released during switchgrass and switchgrass char combustion are summarized in Table 1.

Table 1: Quantification of KCl Released from Switchgrass, Switchgrass Char, and Switchgrass Oils

Sample	Ratio of Areas (39/74)	Ratio of Areas (74/76)	% K Released (as KCl)	Gas Phase K from KCl (ppmw)**
1100° C 20% O_2 in helium				
KCl Standard	3.6	2.5	100	----
Switchgrass	4.1±0.2	2.35±0.18	23.2±4.0	532±62
Switchgrass Char	8.0±0.3	2.6±0.1	36±2	1397±86
Vortex Switchgrass Oil (#146A)*	3.24±1.4	1.31±1.24	23±10	51±23
Vortex Switchgrass Oil (#157)*	3.24±.23	1.46±1.65	63±26	18±7
FBC Switchgrass Oil (Time 0)*	5.16±2.9	1.07±0.11	179±11	36±2
800° C 20% O_2 in helium				
KCl Standard	3.9	2.6	100	----
Switchgrass	4.03±0.31	2.28±0.42	16.5±1.9	378±44
Switchgrass Char	5.8±0.7	2.4±0.1	45±7	1755±280
Vortex Switchgrass Oil (#146A)*	4.2±3.6	1.08±0.65	20±6	44±13
Vortex Switchgrass Oil (#157)*	2.62±1.0	0.85±.27	65±12	23±4
FBC Switchgrass Oil (Time 0)*	3.19±0.93	1.54±0.31	145±62	29±13

The errors are one standard deviation.
*Alkali metal released during switchgrass pyrolysis oil combustion was quantified using the m/z=39 peak (K^+) assuming that this ion came solely from KCl fragmentation.
**Calculated as described in the text below

The largest source of error from this calibration method arises from the variability of the mass spectral signals recorded from the KCl standards. The ratio of the areas under the m/z=74 and 76 time profiles for the KCl standards, the switchgrass, and switchgrass char samples yields, within error, the characteristic 2.47:1 intensity ratio indicative of the natural isotopic abundance of KCl containing ^{35}Cl, ^{37}Cl, ^{39}K, and ^{41}K.[9] The ratio of the areas under the m/z=39 and 74 time profiles for the KCl standards is a measure of the fragmentation of gas phase KCl in the ionizer at a given furnace

temperature. This ratio is slightly temperature dependent.[10] The ratio of the areas under the m/z=39 and 74 time profiles is significantly larger for the switchgrass and switchgrass char samples indicating that other potassium-containing species may be liberated into the gas phase which fragment and are contributing to the signal at m/z=39. Although the majority of the alkali metal liberated during combustion of switchgrass and switchgrass char is in the form of KCl, other alkali metal containing species (presumably sulfates or hydroxides) are also being released.

Using the information from the ultimate analysis of the switchgrass and switchgrass char, it is possible to determine the average %K (from KCl) released into the gas phase. At 1100°C, 36±2% of the potassium in the switchgrass char was released into the gas phase as KCl and at 800°C, 45±7% of the potassium is released into the gas phase. Given the errors in the calibration method, these values are essentially the same. This is a larger fraction, however, compared to switchgrass combustion where only 23±4% of the available potassium is released into the gas phase as KCl at 1100°C and 16±2% of the potassium is released as KCl at 800°C. A more practical way of presenting the amount of alkali released is in parts per million inside a typical combustor. This quantity was calculated by assuming switchgrass and switchgrass char combustion in 20% excess air, conditions that are typical inside a boiler or combustor. The average calculated amount of potassium from KCl released during switchgrass char combustion at 1100°C is 1397±86 ppmw, and at 800°C is 1755±280 ppmw. These values are 2.6 to 4.6 times larger compared to the amount of gas phase potassium released from combustion of the parent switchgrass feedstock at 1100°C (532±62 ppmw) and 800°C (378±44 ppmw).

Similar attempts were made to quantify the alkali metal released during combustion of the switchgrass-derived pyrolysis oils (vortex switchgrass oil (run #146A), vortex switchgrass oil (run #157), and FBC switchgrass oil (time 0)). These results are suspect and less reliable than the results for KCl released during combustion of the solid samples discussed above. Based on the mass spectral results, KCl is the dominant alkali metal containing species released during switchgrass combustion. Individual alkali metal containing species were not identified in the mass spectral results recorded during switchgrass oil combustion (see Figure 7), however, it was possible to identify the K^+ fragment ion. In an attempt to quantify the amount of alkali vapor released during switchgrass oil combustion, several assumptions were made. We first assumed that the dominant alkali metal containing species released was indeed KCl even though it was not identified in the mass spectral results. For these three switchgrass oils, however, it was possible to identify K^+ in the mass spectra, which was assumed to come solely from the fragmentation of KCl. Consequently, the m/z=39 signal (instead of the m/z=74 signal) was used to quantify the alkali metal released during switchgrass pyrolysis oil combustion.

The ratio of the m/z=74 and 76 areas determined from the mass spectral results recorded during combustion of the switchgrass-derived pyrolysis oils are in error compared to the expected ratio of 2.47:1. The signal intensities at these two masses were very low or near zero (see Figure 7), and the areas under the time traces for these ions predominantly consists of the noise. The ratio of m/z=39 and 74 contain the same error. The shortcomings are most prevalent when the percentage of potassium released values are compared for the different switchgrass oils. Twenty percent of the available potassium is released as KCl during combustion of the vortex switchgrass oil (run #146A). This value is similar to the results for combustion of the solid feedstocks. The results for the remaining two switchgrass oils, however, are less reasonable. In fact, for the FBC switchgrass oil more than 100% K is released indicating that either KCl is not the dominant form of the alkali metal released during combustion of these oils, or that the amount of alkali metal released is below the detection limits of the mass spectrometer. Considering all of the potential errors in this quantification method, the amount of alkali metal released during combustion of these oils (assuming combustion in 20% excess air) is believed to be on the order of tens of parts per million. The values in Table 1 for the amount of gas phase K from KCl can be considered upper limits for these oils. Nevertheless,

the switchgrass oils still contain substantially more alkali metal than the recommended specifications (<20 ppb Na and K combined) for gas turbine fuels.[1]

Conclusions

We investigated the combustion of biomass-derived pyrolysis oils and chars to determine the fate of various components of the parent biomass feedstock during pyrolysis oil production. The nitrogen, sulfur, and chlorine content of a given pyrolysis oil is a function of the starting feedstock material. High nitrogen, sulfur, and chlorine-containing biomass feedstocks yield pyrolysis oils with corresponding high levels of nitrogen, sulfur, and chlorine. Based on the results from the present screening studies involving biomass-derived pyrolysis oils and chars, alkali metal is sequestered in the char fines during the production of biomass-derived pyrolysis oils which suggests that efficient filtering should yield a lower alkali metal-containing pyrolysis oil. This result is desirable if pyrolysis oils are to become a competitive fuel for use in turbine combustors for generating power.

Attempts were made to quantify the amount of alkali metal released during combustion of the switchgrass pyrolysis oils and chars. The results suggest that more alkali metal is released during combustion of switchgrass char compared to the amount of alkali metal released during combustion of similar amounts of switchgrass. The amount of alkali metal released during combustion of the switchgrass pyrolysis is at least an order of magnitude lower compared to combustion of the parent switchgrass feedstock. Although the alkali metal levels in the switchgrass pyrolysis oils are lower than the parent switchgrass feedstock, the amount of alkali metal in the oils is still three orders of magnitude higher than recommended specifications for turbine fuels. [1] The levels of alkali metal in pyrolysis oils can be lowered by starting with biomass material having lower alkali metal levels, such as woody feedstocks. For example, the amount of potassium in the poplar oils (vortex poplar oil (run #160) and FBC poplar oil (time 0)) is 30 ppm and 27 ppm, respectively which is considerably lower than the potassium levels in the switchgrass oils. Even with these potential improvements, it will be difficult to produce biomass-derived pyrolysis oils with acceptable levels of alkali metal as required by manufactures of gas turbines for fossil-derived fuels. Whether such stringent criteria will apply to biofuels remains to be determined.

Acknowledgements

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APPLIED BIO-OIL COMBUSTION

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ABSTRACT

As the conversion of biomass to liquid fuels via fast pyrolysis becomes an economic reality, interest is being focused on applied bio-oil combustion. Research efforts are addressing storage and delivery systems, bio-oil/petroleum blending, burner modifications and combustion optimization for emissions control.

While current fast pyrolysis bio-oils appear unattractive when compared only with highly refined distillate fuel oils they represent a significant improvement when viewed as alternatives to the widely utilized traditional biomass fuels, black liquor and hog fuel.

Practical aspects of bio-oil combustion are presented based primarily on experience with the 20 million BTU per hour combustor located on the site of Ensyn's 25 tonne per day commercial RTP™ plant. This industrial swirl burner was installed in 1988 and operates continuously on a mix of pyrolysis bio-oils, char and combustible pyrolysis gases. A heat exchanger provides hot air for plant heating and particulate is collected in a standard baghouse. Recent stack tests for CO, NOx and formaldehyde confirmed that emissions were only a fraction of permit levels.

1.0 INTRODUCTION

In the quest for more effective utilization of biomass resources for energy the thermochemical conversion technology known generically as fast pyrolysis has gained increasing prominence. Several processes have been brought to demonstration or commercial status. With the availability of barrel quantities of the liquid pyrolysis products (bio-oils) interest is being directed toward the practical aspects of applied combustion. In addition to on-going small-scale laboratory tests, several extended tests have been carried out in flame tunnels, combustors and boilers, including work at MIT (U.S.A.), CCRL (Canada), SANDIA (U.S.A.), ENEL (Italy) and NESTE (Finland). Combustion of traditional slow pyrolysis derivatives is practiced on a commercial basis by at least two U.S. based manufacturers of food (smoke) flavourings, one of whom has also been burning fast pyrolysis liquid fuels for over two years.

2.0 FUEL CHARACTERISTICS OF PYROLYSIS BIO-OILS

A number of research, pilot plant and commercial systems are now converting biomass feedstocks to liquid fuels utilizing different approaches to fast pyrolysis. There can be a wide variation in bio-oil properties depending on the feedstock selected, the process conditions utilized and the degree of upgrading applied either during or after production. However, for a given selection of these parameters, the variation is relatively minor and a reasonable set of fuel characteristics can be listed. Table 1 gives values for an RTP™ bio-oil that is generally consistent with anticipated near-term commercial production. Also included are representative fuel characteristics for those conventional biomass fuels in greatest use at the present time. Hog fuel (a solid biomass fuel) and black liquor (a thermochemically derived liquid bio-fuel) are the major fuels used in the pulp and paper industry.

If fast pyrolysis bio-oil is compared to hog fuel the general improvement in fuel properties is immediately evident. The water content of bio-oil is less than half that of hog fuel and the ash content is an order of magnitude lower. With the heating value of bio-oil roughly double that of conventional hog fuel and the density dramatically increased by the conversion from a solid to a liquid, the energy density of the pyrolysis fuel becomes 5-6 times greater than that of the original biomass. Nitrogen and sulphur levels are comparable, leaving only the acidic nature of the bio-oil as a significant negative factor.

Similarly, when compared to the traditional thermochemically produced, biomass derived liquid fuel (black liquor) the fast pyrolysis bio-oil is a generally superior fuel. The water content is significantly lower, the density is slightly higher, the viscosity is lower and the heating value is roughly double. In addition, both the ash and sulphur contents are approximately two orders of magnitude lower in the pyrolysis bio-oil. The black liquor is highly caustic and therefore, presents as great a handling problem as the mildly acidic bio-oil.

If comparisons are limited only to the highly refined distillate fuel oils, then the current fast pyrolysis bio-oils appear unattractive; however, if viewed in relation to the traditional biomass fuels (of which millions of tonnes are combusted annually) pyrolysis bio-oils quite clearly represent a significant improvement in overall fuel quality.

Table 1 CHARACTERISTICS OF BIOMASS FUELS

PROPERTY	HOG FUEL	BLACK LIQUOR	BIO-OIL
Water Content (wt%)	45-55	30-40	18-24
Ash Content (wt%)	1-5	20-30	0.03-0.15
Density (g/ml)	0.25-0.40	1.078	1.19-1.23
Viscosity (cst)		220-400	120-250
Higher Heating Value (MJ/kg)	8-12	8-10	17-19
pH		11-13	2.6-3.3
Elemental (wt%, MF)			
Carbon	47-52	45-50	52-58
Hydrogen	5-6	4-5	6-7
Nitrogen	0.10-0.30	0.05-0.20	0.05-0.30
Sulphur	0.02-0.10	3.0-4.0	0.005-0.05

3.0 INDUSTRIAL COMBUSTION OF PYROLYSIS BIO-OILS

Red Arrow Products of Manitowoc, WI (a large commercial producer of smoke flavourings through biomass pyrolysis), purchased a solid fuel swirl burner from Energy Control Engineering Minnetonka, MN in the early 1980's. This unit burned by-product char and was installed to replace an existing natural gas-fired burner that provided process heat for a rotary drum sawdust drier. Based on the excellent performance of this unit (payback period of approximately one year) a second swirl burner was purchased and commissioned in April of 1988.

3.1 Fuels

This 20 million BTU/hr swirl burner was designed to utilize a combination of by-product fuels including char, non-condensible combustible gases and bio-oils (after stripping of food chemicals) from both conventional slow pyrolysis and RTP™ fast pyrolysis. A summary of fuel characteristics is provided in Table 2.

Table 2 **INDUSTRIAL BURNER FUEL CHARACTERISTICS**

	MC (wt%)	HHV (BTU/lb)	DENSITY (s.g.)	VISCOSITY (cp)	SOLIDS (wt%)	ASH (wt%)
char	0.5	11800	0.22	NA	NA	4.0
gases	3.0	2222	NA	NA	NA	NA
RTP™ bio-oil residuals	12.1	9673	1.22	1500@65°F (est)	10.0	1.5
Slow pyrolysis bio-oil residuals	12.6	11427	1.16	500@65°F	<1.0	0.05

The proportions of the three fuel types (solid, liquid, gaseous) vary widely depending on the plant operations, but a typical daily average would be:

CHAR	1000 lbs/hr	11,800,000 BTU/hr
GASES	200 "	440,000 "
BIO-OILS	740 "	7,760,000 "

3.2 Combustion

The swirl burner (West Waste Fuel Burner) was designed by Bill Webb of Energy Control Engineering. It is a refractory lined cylindrical combustor with a height of 24 feet and internal diameter of about 9 feet. Four stainless steel blowers vertically spaced on one side of the unit provide the combustion air. The tangential air inlets create a swirl pattern in the combustor that ensures fuel/air mixing for good combustion. The air flows from the blowers can be manually adjusted using a thermocouple located in the top of the combustor as the controlling indicator (supplemented by periodic tests for stack emissions of CO).

The unit is started by lighting wood shavings placed in the bottom of the combustion chamber. Once a fire has been established, the char feed is activated to increase the fire intensity. When the combustion chamber temperature has reached at least 1100°F, the bio-oil and gases can be introduced. Typically the three fuel types are fed continuously, 24 hours per day.

3.3 Fuel Delivery

Char is fed via three tangential ports located at 1, 3 and 5 feet above the base of the combustor. Augers convey the char from a storage bin to a pick-up trough where a stainless steel blower provides an air flow to pneumatically transport the char through 3-inch pipes to the injection ports.

Non-condensible fuel gases from the plant operations are drawn into the combustor by the negative pressure from the systems induced-draft exhaust fan. Normally only about 10% of the plant by-product gases are directed to the swirl burner in order to maximize consumption of char

and bio-oils.

Bio-oils (heavy liquid residuals after food chemicals removal) from both slow and fast pyrolysis are stored in 4000 gallon stainless steel tanks which are enclosed but not sealed. The bio-oil is delivered to the combustor by a variable speed positive displacement pump at a base pressure of 20 psig. An in-line strainer with 0.25 inch openings prevents large solids from plugging the burner nozzle and a Foxboro flow meter is used as the indicator for adjustment of pump speed. The discharge pressure is monitored and when it exceeds about 50 psig the burner nozzle is removed and cleaned (approximately every two weeks). The stainless steel line from the pump to the combustor is steam traced which provides a bio-oil preheat of about 130°F.

3.4 Bio-Oil Burner

The bio-oil burner utilizes a Ripco stainless steel nozzle which has four quarter-inch orifices. Atomization air is directed through a concentric line of the burner assembly and mixed with the fuel at the nozzle outlet (approximately 21 SCF of air per U.S. gallon of bio-oil). The pressure of the air is maintained at 20 psig above the oil pressure. A diaphragm sealed pressure gauge and variable regulator achieve the necessary control. The oil line is fitted with a check valve to ensure that no air backs up the oil line. The injection point of the nozzle is located at one of the primary air blowers to immediately disperse the incoming oil and keep the nozzle tip relatively cool. The current nozzle has been in use for 3 years.

3.5 Heat Recovery and Ash Collection

A 6000 square foot exhaust gas to air heat exchanger is located at the combustor exit and provides all space heating needs of the plant. The exhaust gas temperature is reduced to below 500°F after the heat exchanger (with extra ambient air dilution if required) which allows the exhaust to pass through a baghouse where ash is removed to meet particulate emission levels. The dry ash collected can be used as a filler in concrete (the Red Arrow parking lot concrete contains 5-10% ash), sent to landfill or spread on agricultural land as a fertilizer/neutralizing agent (up to 2 tons per acre is allowable).

3.6 Emissions

In June 1994 Red Arrow had emission tests conducted on the West Waste Fuel Burner by a certified testing firm in accordance with regulations of the Wisconsin Department of Natural Resources. Tests were carried out for Carbon Monoxide (CO), Nitrogen Oxides (NOx) and Formaldehyde. Measured levels were only a fraction of the permitted emission rates for the combustor. Emissions of CO were 17% of the permitted rate, for NOx only 1.2% of the permitted rate and formaldehyde emissions were not detected (indicating less than 0.2% of the permitted value).

3.7 Maintenance

Maintenance requirements on the combustion system have not been excessive. The bio-oil injection nozzle is cleaned about every two weeks, ash in the base of the combustion chamber is broken up and removed about every two months and the heat exchanger is cleaned once per year.

4.0 NOZZLE TESTS

Previous tests in small household burners (at Ensyn and at CANMET) had established that RTP™ bio-oils could be mechanically atomized (pressure nozzles) provided that char levels were very low and sufficient preheating was achieved. In preparation for retrofitting a small industrial boiler located at Ensyn, several preliminary nozzle tests were carried out to establish the effect of preheating on flow rates achieved for standard pressure atomization nozzles.

Figures 1 and 2 show plots of cumulative mass of bio-oil versus time for a standard 12 gallon (U.S.) per hour 60° nozzle operating at 100 psig, for preheat temperatures of 60 and 90°C respectively. In both tests there was an initial decrease in the flow rate over the first few minutes after which the flow rate remained reasonably steady. A straight line regression analysis for the stable portion gave flow values of 4.8 gallons per hour at 60°C (40% of the nozzle rating) and 7.1 gallons per hour at 90°C (60% of the nozzle rating).

5.0 FUTURE ACTIVITIES

Several near-term tests will be conducted as part of Ensyn's on-going efforts to acquire more information on practical aspects of bio-oil combustion. A sample of RTP™ bio-oil from the commercial plant at Red Arrow has been sent to MAXON Corporation, Muncie, PA. for evaluation in their dual fuel burners. It is expected that tests will include co-firing with natural gas and with heavy oil (No. 6).

A pump skid and injection lance have been assembled to provided a 30-50 gallons per hour supply of bio-oil to a 90 million BTU/hr coal-fired moving grate utility boiler. Test firing of bio-oil (at 4-5% of thermal input) will be carried out in early 1995 at the MPU.

Also scheduled for early december is a bio-oil combustion test in the flame tunnel at CANMET, Ottawa. This 6-hour burn will be monitored by a certified private emissions testing firm who will test stack emissions for CO, SOx, NOx, particulate, metals, dioxins and furans, PCB's, PAH's, VOC's and chlorinated aromatics.

6.0 SUMMARY

Fast pyrolysis bio-oils, even at their present early stage of development, represent a significant improvement over the conventional biomass fuels (black liquor and hog fuel) already being utilized on a large scale in industrial combustion systems. Industry experience has clearly shown that bio-oils can be stored, pumped, heated and burned in commercial systems without undue difficulty or excessive maintenance requirements. Emission levels are well below EPA/State permit regulations when normal control technology is applied.

FIGURE 1: Cumulative Mass of Bio-Oil vs. Time.
(12 USGPH Nozzle, 90°C, 100 psig)

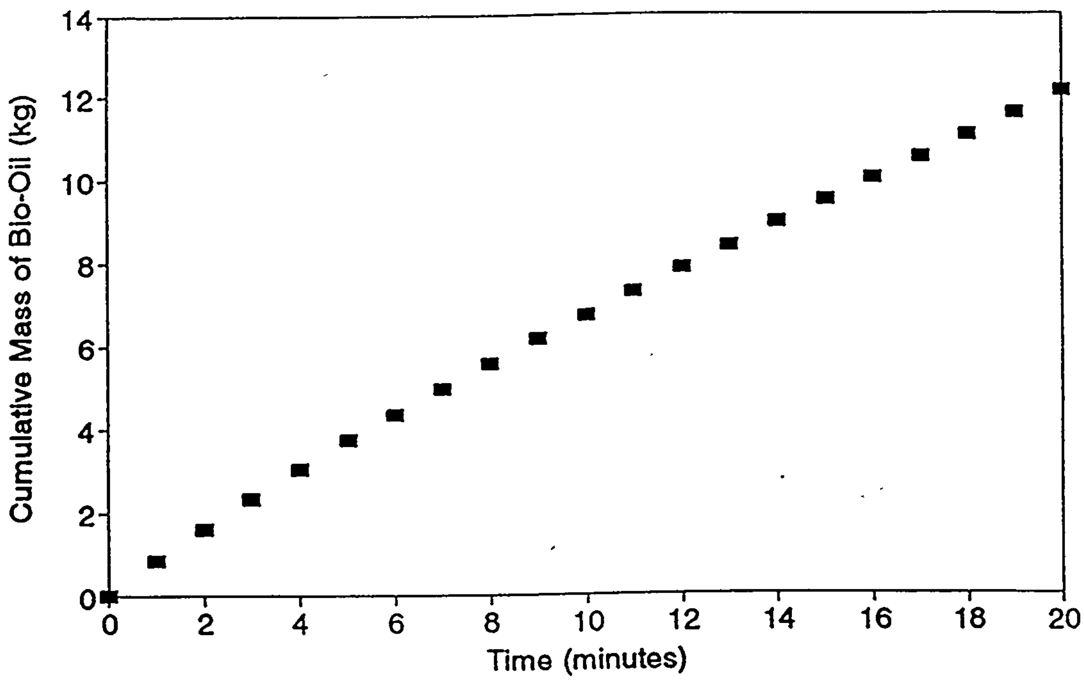
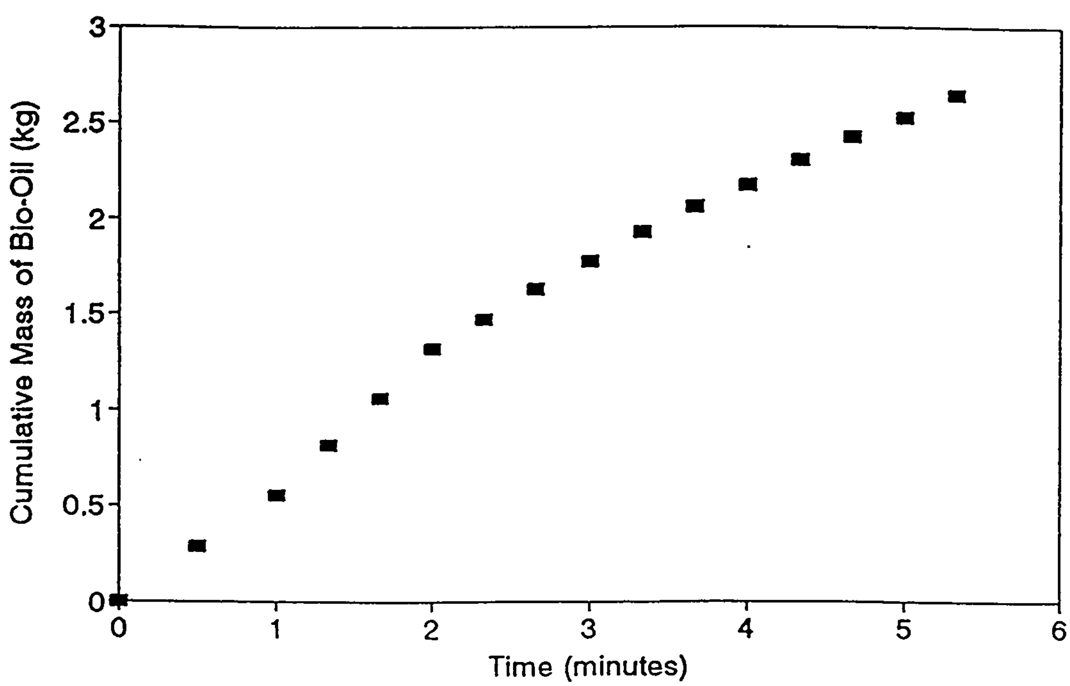


FIGURE 2: Cumulative Mass of Bio-Oil vs. Time.
(12 USGPH Nozzle, 60°C, 100 psig)



FLASH PYROLYSIS FUEL OIL

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ABSTRACT

Background

This project investigates the possibility of utilizing flash pyrolysis oil as a light fuel oil substitute for institutional customers such as schools, hospitals and small industry etc, where we currently market Tempera 15. Tempera 15 is priced and has technical properties between that of low sulphur heavy fuel oil and residential type fuel oil. It has viscosity of about 15 cSt at 20°C, requires preheating to 50 °C and a storage temperature above 10°C. It sells for about 1.3 mk/1 (0.25 USA/1) which includes tax of 0.4 mk/1.

FUEL CLASSIFICATION

Flash pyrolysis oil has the potential to be used as a fuel in boilers, gas turbines or diesel engines. It can be made from a variety of feedstocks under various reactor configurations and with different recovery and post-production treatment sytems. This leads to differences in product quality due to changes in water, char and ash content, pH, viscosity, fuel nitrogen, and heating value. These in turn lead to differences in chemical, physical and combustion properties of the liquid product. The extent of these differences and their effect on product quality is the subject of this and related studies. Based on present knowledge of crude flash pyrolysis properties, it can be roughly classified somewhere between light fuel oil (LFO) and low sulfur heavy fuel oil (LSHFO). In general it contains less sulphur, is less viscous and has a lower pour point than heavy fuel oils and under appropriate conditions can be combusted with simple mechanical atomization equipment.

But compared to light fuel oil it has the following drawbacks:

1. difficult to ignite
2. high viscosity
3. low energy content
4. poor stability when exposed to air or high temperatures
5. low pH, corrosive and poor lubricity
6. higher emissions using simple mechanical atomization

While some of these problems can be controlled by choosing appropriate equipment and materials, it is unlikely that untreated, primary flash pyrolysis oil could meet the

requirements of a residential heating fuel oil. Replacement of heavy fuel oil is possible but this would be economically more difficult (see below).

But there is a market segment in Finland as well as in other countries where light fuel oils are combusted where many of the problems of flash pyrolysis oil could be effectively handled. These are industrial size boilers in the intermediate size range, from about a few 100 kWs to a few MWs that are used for heating and hot water systems for schools, blocks of flats, hospitals, office complexes, small industry etc. The light fuel oil grade that primary flash pyrolysis oil has the potential to replace in Finland that is marketed by Neste Oy is Tempera 15. Tempera 15 is priced and has technical properties between that of LSHFO and LFO. It has viscosity of 15 cSt at 20 °C, 0.2% sulphur, requires preheating to 40-50 °C to ensure good atomization and a storage temperature above 10 °C. Minimum delivery volume is 7000 liters. It sells for about 1.2-1.3 mk/l (0.23-0.25 USD/l) which includes tax of 0.37 mk/l.

ECONOMICS

The market price for light and heavy fuel oils in Europe is shown below. The non-taxed price for light fuel oil varies from 0.18-0.27 USD/l with most countries under 0.2 USD/l. This includes feedstock, margin and distribution costs. This is for fuel oil at about 36 MJ/l LHV which corresponds to about 0.10-0.14 USD/l for flash pyrolysis oil at 19 MJ/l LHV. The non-taxed price for heavy fuel oils varies from 9-12 US cents/kg in most countries in Europe with a corresponding market "value" for flash pyrolysis oil of about 4-6 US cents/kg. Sweden has recently introduced high environmental taxes which has increased the cost of fuel oils (although rebates to industry are possible) which makes biomass derived products that receive tax exemptions more competitive. The heavy fuel oil in the figure for Finland is low sulfur (<1%) which starting from 1993 must be used in southern Finland inboilerswithout sulfur removal equipment. Prices for other grades of fuel oil such as Tempera 15 fall in between that of light and heavy fuel oils.

A preliminary economic analysis of flash pyrolysis oil production costs was performed. The base case feedstock cost used for this study was the cost target for delivered biomass from the Finnish Bioenergy Program. This study showed that potential exists in Finland to profitably produce flash pyrolysis oil as a Tempera 15 replacement when the following conditions are met: 1. the delivered price of woodchips is $\leq$ 45 mk/MWh (50 USD/dry tonne,) 2. flash pyrolysis oil is sold at 0.76 mk/l (equivalent to price of fuel oil at 1.3 mk/l on energy basis) and 3. product will be taxed at the same level as wood fuels today (=0).

Flash Pyrolysis Oil Samples at Neste

Two samples from Ensyn Technologies Inc. of Canada were tested. The first

sample (Ens93) had higher water content (26 vs 19 wt%), higher solids content (2 vs 0.6wt%) and lower viscosity (15 vs 100 cSt @ 50 °C) than the second sample (Ens94).

Preliminary analysis for EPA-PAH of ENS93 gave concentration levels similar to or lower than that of Tempera 15 light fuel oil depending on the source of crude. Procedures similar to that for hydrocarbon samples were used and at other

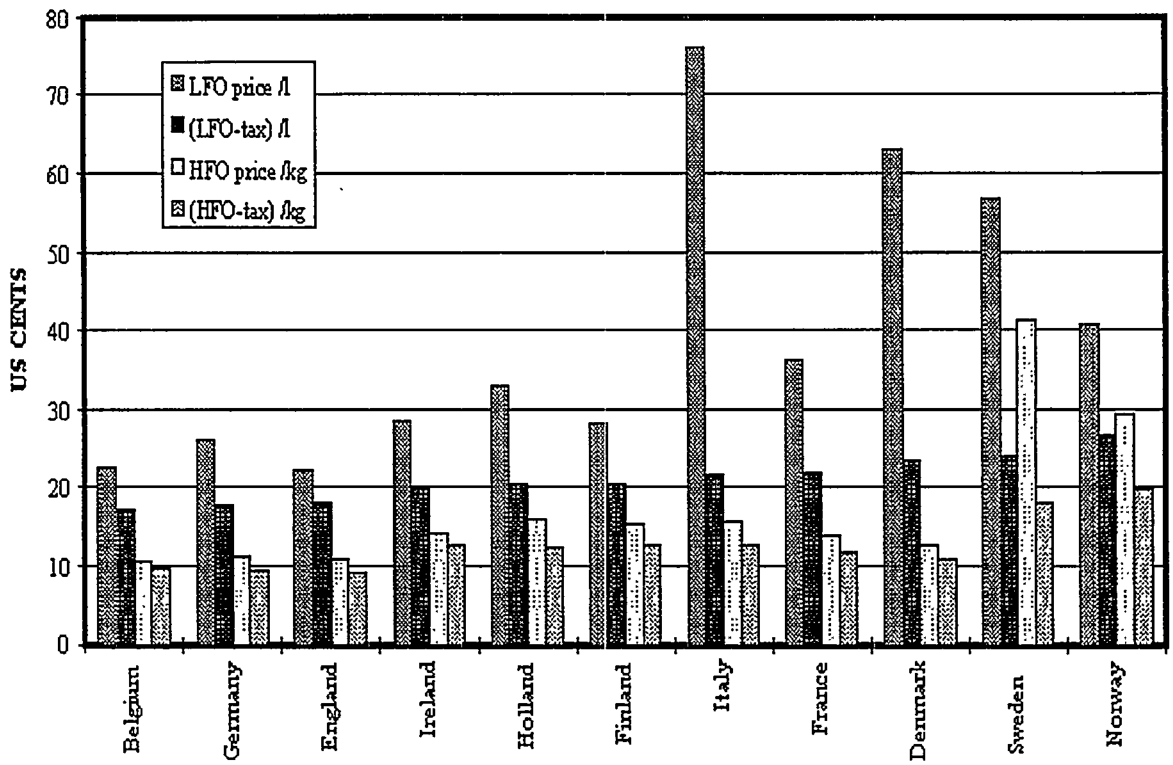
procedures are being tested. But results compared to that for slow pyrolysi oil clearly inicated much lower levels, on the order of 3-5%.

Combustion Experiences

1. Fall 93

Initial combustion testing was performed on Ens93 in a district heating type 2.5 MW Danstoker boiler fitted with a dual fuel burner using normal pressure atomization allowing the simultaneous combustion of flash pyrolysis oil with light fuel oil at

FUEL OIL PRICE COMPARISON, 1994



different ratios. The boiler was equipped with quartz windows which allowed flame shape and flame quality to be observed.

Initial tests with unfiltered flash pyrolysis oil caused pump pressure to fluctuate by ± 3 bar and stable combustion could not be obtained. The oil was then filtered to 35 microns. During filtering it was noted that char particles had settled to the bottom of the barrels during storage which caused filters to block so that only the top two thirds

of the barrel could be used. In the first series of tests, various light fuel oil and flash pyrolysis oil ratios as well as nozzle types, excess air amounts, preheat temperatures, oil pressures were tested in order to observe flame shape and quality. The flash pyrolysis oil was not able to combust on its own under these conditions. The conclusion from these tests was that flash pyrolysis would not ignite in this type of cold walled boiler. A radiative heat sink was required to assist in the evaporation of the water in the oil and maintain flame temperature.

In the next set of tests, a metal tube approximately 1 meter long x 1/2 meter diameter made from sheet metal was inserted into the boiler and warmed up with light fuel oil. This type of heat radiating surface allowed ignition and short term combustion of flash pyrolysis oil but was found to cool rapidly and as it cooled, the flame extinguished. During these initial tests it was noted that the pyrolysis oil flame was composed of two sections. The first section, close to the nozzle was presumably from the combustion of light, volatile components of the pyrolysis oil while the second section was of the char combustion.

The insert was then wrapped with insulating material. The flash pyrolysis oil was now found to be able to combust on its own without an auxiliary fuel. It was not possible to carry out long term combustion testing in this configuration due to lack of sample but emissions (CO, NOx and particulates) plus excess air was used to follow the effect of pump pressure (8-14 bar), fuel preheat (50-80 °C) and combustion air changes (2-8% O_2). The emission levels were found to vary considerably with parameters tested with the best results that were obtained were: NOx <140 ppm, CO < 90 ppm and particulates with a Bacharach number of 6-7 . The particulate result also showed a partial yellowish-brown colour which is different than for normal fuel oils.

2. Fall 94

In the second set of tests, Ens94 sample was used. An Arimax Eetta 200 kW boiler was fitted with a precombustion chamber of dimensions approximately 1 meter long by 0.5 meter diameter. A commercial dual fuel burner Oilon KP24H was modified so that combustion air could be set manually. A 1 kW preheater was used to adjust Ens94 from between 70-90 °C. It was found necessary to warm Ens94 prior to pumping since room temperature viscosity was approximately 1000 cSt. Danfoss nozzles were chosen such that the volume ratio of Ens94 to Tempera 15 was roughly 2:1 to assist in air adjustments when switching from the mineral oil to pyrolysis oil. Typical results for Tempera 15 are in Table 1. Oil pressure was 10 bar and a Danfoss 1.75 gal 60°S nozzle was used.

Table 1. Combustion of Tempera 15

02 %	CO ppm	NOx ppm	Bacharach	oil T	chamber T
2.7	14	128	1.2	24	900
4.3	14	115	1.2	24	880
6.1	10	111	1.5	24	870

For Ens94, oil pressure was set at 15 bar and some initial results for a 2.25 gal. nozzle

are shown in Table 2. Both particulates and carbon monoxide were found to be higher than for Tempera 15. For Ens94, optimized conditions are pump pressure >15 bar, oil preheat > 80 °C, combustion chamber warmed to > 900 °C .

Table 2. Combustion of Ens94 in 200 kW boiler.

O2 %	CO ppm	NOx ppm	Bacharach	oil T	chamber T
3.5	80	160	6	85	930
5.8	72	215	4	75	940

Observations

1. In the boiler configurations tested to date, particualtes, NOx and carbon monoxide are all higher from flash pyrolysis oil than for the equivalent fuel oil under similar conditions. NOx emissions will have significant contributions from fuel nitrogen depending on feedstock. Simultaneous high particualtes and CO indicates incomplete combustion which must be addressed by further improvements of atomisation.
2. Flash pyrolysis oil will not undergo self-sustaining combustion at cold temperatures and after shutdown product remaining in lines will form tars and coke that will block nozzles. This means that an auxiliary fuel will be required.

Conclusions

1. Flash pyrolysis oil can be combusted using simple mechanical atomization equipment with proper optimization of combustion conditions.
2. Flash pyrolysis oil requires improvements in fuel properties/atomization and combustion conditions when compared to a similar grade fuel oil, Tempera 15.
3. For profitable production of flash pyrolysis oil in Finland using forestry residues with a delivered price of 5 US cent/dry kg (Finnish bioenergy program goal) would require that no costly upgrading is required to fulfil technical demands and that fuel tax level is the same as that for wood (=0).

BIO-OIL COMBUSTION TESTS AT ENEL

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ABSTRACT

ENEL–Thermal Research Center (CRT) is involved in a research program aimed at assessing the feasibility of utilizing bio-fuels derived from flash pyrolysis of vegetable biomass as a fuel in furnaces, gas turbine combustion chambers and other energy applications.

In the past some preliminary combustion tests have been already performed by ENEL, firing bio-oil produced through a conventional slow pyrolysis process, in a commercial type burner for liquid fuel.

With the construction and operation of a 15 t/d flash pyrolysis plant in Umbria Region, next year ENEL will be able to carry out more comprehensive tests in this field.

In the meanwhile CRT has performed combustion tests utilizing relatively small quantities of bio-oils supplied by Spanish and Canadian producers.

These tests are aimed at investigating the atmospheric stationary combustion of crude bio-oil and the pressurized combustion of different bio-oil/ethanol mixtures, directly in a small gas turbine combustion chamber.

Tests include accurate bio-fuel chemical and physical characterization, flame investigation, combustion process assessment and characterization of flue gas.

A 0.5 MWth furnace and a 40 kWe gas turbine are the experimental facilities, located in the ENEL Experimental Area of Livorno, that are used for the execution of the above mentioned trials.

In parallel to these tests, ENEL has commissioned to MIT-Combustion Research Group of Boston, combustion tests on the same type of bio-fuels fired in Livorno, to be performed with a burner optimized for minimum NO_x production, with a heat input ranging from 1 MWth to 0.25 MWth, to simulate turn-down.

The major part of research activities presented are conducted with the financial support of EEC.

The results of tests will be useful in particular to evaluate the potential and the limitations of direct crude bio-oil utilization, without complex and expensive upgrading processes.

INTRODUCTION

Biomass pyrolysis oil is a particular off-spec fuel whose penetration into the market as substitute for conventional fossil fuels to produce electricity strongly depends upon the standards of its characteristics.

Large R&D efforts are progressing to get a better understanding of the production processes, the chemical-physical characterization, and the final use in furnaces, combustion chambers of gas turbines or in diesel and reciprocating engines, with the final goal to produce electricity from renewable resources.

ENEL–CRT is actively involved in the field of biomass pyrolysis oil through several research activities, the major part of them financially supported by the European Union.

In particular, the most important project of this sector is represented by the construction, in collaboration with Umbria Region, of a flash pyrolysis plant supplied by Ensyn (Canada), to be erected at ENEL's Bastardo (Perugia) power plant, in the center of Italy (1).

The plant will be capable of producing around 500 kg/h of crude bio-oil, processing 15-20 t/d of dry feedstock, namely hardwood, but with the possibility of processing other sorts of biomass, such as sorghum, mischantus, etc.

The construction of this plant, which will be operational in the second half of next year and will be the largest plant in Europe, is of great relevance for assessing an advanced pyrolysis process. Because of the availability of so large an amount of bio-oil, we will carry out a more significant research activity in regard to characterization, storage, handling, upgrading, combustion and pollution control in the electricity production process.

It will be possible to overcome the actual limitations posed by the scarcity or inadequate supply of bio-oil, and by the high cost of the product, to conduct a more comprehensive R&D activity.

After the first preliminary tests, including characterization and combustion trials, it appeared necessary for a more in-depth investigation on the properties of bio-oil, in view of its commercial application.

In addition to the chemical-physical characterization and the advanced thermal analysis, combustion tests demonstrated the need for further investigations, especially on the rheology of the fuel, to optimize the burners feeding system, taking into account the severe operating conditions because of the acidity and the corrosion potential of these products.

BIO-OIL CHARACTERIZATION

The first approach of ENEL–CRT in the field of bio-oil characterization has been the chemical-physical analysis of crude bio-oil produced by different suppliers: BioAlternative (CH), Ensyn (Canada) and Union Fenosa (Spain).

These analysis have been faced and afforded on the basis of the former ENEL's experience on conventional fossil fuels; suitable methods requested by the peculiar fuel are under investigation, especially in regard to the water content.

On many occasions the necessity of standard methods has been stressed to reach homogeneous results of laboratory investigations.

ENEL has extended its investigations with bio-oil to thermal analysis, which has been performed by heating the sample both in oxidant and reducing environment, and recording the response to thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA).

Figure 1 shows the behavior of bio-oil when heated in an inert environment, in comparison with heavy oil.

Also a coking index has been determined by thermogravimetry; this index represents the percent of coke residue after rapid heating in an inert environment and is considered a valuable indicator of the liquid fuel burnability.

Thermal analysis shows that bio-oil is a less homogeneous product than fuel oil because it includes different light and heavy fractions. Through the coking index it was possible to extrapolate the asphaltenes content, while DTA allowed us to evaluate the incipient ash fusion temperature. The ash analysis exhibits a high sodium content, which agrees with the low fusion temperature.

At ambient temperature a small quantity of suspended solid material, difficult to be quantified, is present; it is made of particles of different size, up to some millimeters.

Evaluating these impurities is very important for operating the equipment, such as furnaces, boilers or combustion chambers, because impurities can affect the operating conditions by plugging the atomizing tips.

PRELIMINARY COMBUSTION TESTS

ENEL performed the first bio-oil combustion tests in 1991, using about 15 t of bio-oil produced by BioAlternative, through a conventional slow pyrolysis process (2). It was a first attempt, performed in collaboration with ERSA of Region Abruzzo, aimed at verifying the burnability of oil.

As a matter of fact, these tests proved the feasibility of firing crude pyrolytic bio-oil in a commercial burner (0.65 MWth) with mechanical atomization, suitably adapted to the specific fuel, in particular one with a high oxygen content in respect to the usual fuel oil, which achieved a stable combustion. Tests were performed at a flow rate of 105 kg/h, corresponding to 0.5 MWth.

Oil has been heated up to 80°C to reach the required viscosity. Optimization of parameters was reached by monitoring CO vs. the excess of air in different flame patterns, obtained by changing the size and type of atomizing tips, the position of the swirler, and the fuel pressure (around 19 bar).

Tests demonstrated the burnability of bio-oil. The control of pollutants in flue gas showed NO_x and CO concentrations similar to the figures typical of fuel oil combustion. The SO_2 content was directly correlated to the low sulphur content of bio-oil. The particulate matter in the flue gas was intermediate between light and heavy oil (Figure 2). Also a preliminary investigation PAH emissions was performed with satisfactory results.

The problems experienced during these tests were those related to the use of components, such as the pumps and the valves, which were made of common materials not suitable for withstanding the severe corrosion problems encountered in preliminary laboratory tests. These tests were carried out for a period of about 400 hours, at two different temperatures: 25°C and 60°C.

At ambient temperature, the common steels exhibit corrosion rates about 1,7 mm per year, whereas the austenitic stainless steels exhibit a complete resistance to the corrosive agent, which is also maintained at a higher temperature (Table 1).

These first results, if obtained with bio-oil not produced through a flash pyrolysis process, were very useful for focusing attention on the main problems encountered when firing such fuels. They proved useful for the further approach with bio-oil of specific interest.

FLASH PYROLYSIS CRUDE BIO-OIL COMBUSTION TEST

ENEL–CRT is carrying out combustion tests using different bio-oils produced through flash pyrolysis processes. Interest is now focused on this kind of bio-fuel because it is obtained in processes exhibiting higher liquid yield production in comparison with conventional slow pryrolysis.

The tests in progress or recently accomplished are divided into different tasks and are mainly performed with the financial support of EEC (contract JOUB CT92 0100) (3).

Bio-oil direct firing

This work assesses the combustion of crude bio-oil in atmospheric stationary conditions. The combustion tests are being conducted in an experimental facility already available at ENEL's Experimental Area of Livorno.

The vertical furnace, with a thermal capacity of 0.5 MW, is a multi-purpose test rig that can be fired with pulverized coal, fuel oil, coal-water slurries (CWS) and gas. The burner, located on the top of furnace, is derived from an industrial swirl type design. Some minor modifications were necessary to adapt the facility to the particular scope of the research.

The existing CWS piping and fittings have been used, with the addition of a nitrogen-sealed stainless tank, equipped with a stirrer, and a Moyno volumetric pump to take into account the special chemical-physical properties of bio-oils.

During the tests, the following parameters are investigated:

- Furnace thermal load
- Final 0_2

A number of data are collected during the operation:

- Operating conditions (flow rates, temperatures)
- Flue gas sampling and chemical analysis (NO_x, CO, SO_2, CO_2)
- Solid particles sampling

Gas turbine combustion test

These tests verify the possibility of using bio-oils in a gas turbine combustor. The task is not easy because of the particular properties of crude bio-oil, characterized by a low H/C ratio, a high content of oxygen and water, asphaltenes, phenols and exhibiting high density, viscosity and acidity.

All these factors pose handling and combustion problems that could be mitigated by the upgrading the bio-oil or by mixing it with ethanol. A suitable combustion can be reached with a proper injection system, different from those used for the usual liquid fuels, to provide a satisfactory combustion efficiency and a good flame stability.

The experimental matrix includes using ethanol/bio-oil mixtures with different ratios, simulating the conditions existing in a turbogas combustion chamber.

For this purpose an experimental rig has been set up, including the combustor of a small 40 kWe gas turbine, for investigations initially limited to the combustion process. The rig, which is pressurized, is depicted in Figure 3. It includes a critical nozzle for pressurizing the combustion chamber and a heat recovery combustion air preheating system. The main fuel pumps are provided with a continuous control flow regulation. An electrical heater is located downstream of the bio-oil pump.

The operating conditions of the plant are as follows:

Combustion chamber pressure	max 3 bar
Inlet air temperature	150°C - 200°C
Flue gas temperature	700°
Combustion air flow rate	max 1000 kg/hr
Fuel flow rate	max 30 kg/hr
Bio-oil temperature	90°C

The test rig instrumentation has been designed to measure combustor performance and includes thermocouples, pressure sensors and sample probes for a Mobile Emission Control Laboratory (continuous monitoring of O_2, CO, CO_2, NO/NO_x and SO_2.

The activity in progress concerns investigating the influence of the spray chemical-physical properties related to the different types of fuel: kerosene, ethanol and bio-oil/ethanol mixtures.

The reference fuel is kerosene: the results with this fuel will be compared with the combustion of ethanol and different ratios of ethanol/bio-oil mixtures.

Atomization

The combustion of bio-oils both in atmospheric burners and in pressurized gas turbine combustors requires non-conventional atomizers to take into account the special chemical-physical properties such as viscosity, surface tension and water content, which do not allow optimized atomization performances with the normal nozzle geometries.

On the basis of experience of CRT in this specific field, ENEL has studied two different types of atomizers for the combustion chamber of the gas turbine, which will replace the conventional dual fuel atomizer an "effervescent" atomizer and an internal-mixing nozzle. Both atomizers are designed with an additional injector of ethanol atomized with air.

Another special Y-mixing atomizer has been designed for burning bio-oil in the 0.5 MWt furnace of Livorno to perform the combustion tests related above.

The quality of the spray in the new atomizers is evaluated with a Phase-Doppler Particle Analyzer which uses water instead of bio-oil because of the difficulties in simulating the fuel with other commercial liquids.

First results

After an overall set up of the experimental rig, the combustor has been characterized by firing kerosene and ethanol and investigating the effect of pressure, temperature, residence time, spray diameter, etc. on the quality of emissions.

First runs on the combustion of bio-oil have only been performed for a very short duration because the original injector clogged because of the small holes (0.8 mm diameter) and the unsuitable mechanical atomization system.

The first sample of bio-oil used was one supplied by Union Fenosa. Bio-oil homogeneity has been assured by stirring the fuel in the tank and by means of an external recirculation.

Handling ethanol has posed no problems, whereas the pumping exhibited some difficulties such as frequently plugging the filter, and difficult control of flow rate, especially at lower values and with oil heated up to 80°C.

Ignition difficulties and significant carbonaceous deposits of unburnt material inside the combustor have been noticed. To carry on the tests two new injectors have been designed with larger holes and with air assisted atomization of fuel.

Changing the injector also required designing a new combustor to replace the original one. Three nozzle configurations with different diameters have been tested: 15 mm, 20 mm and 25 mm.

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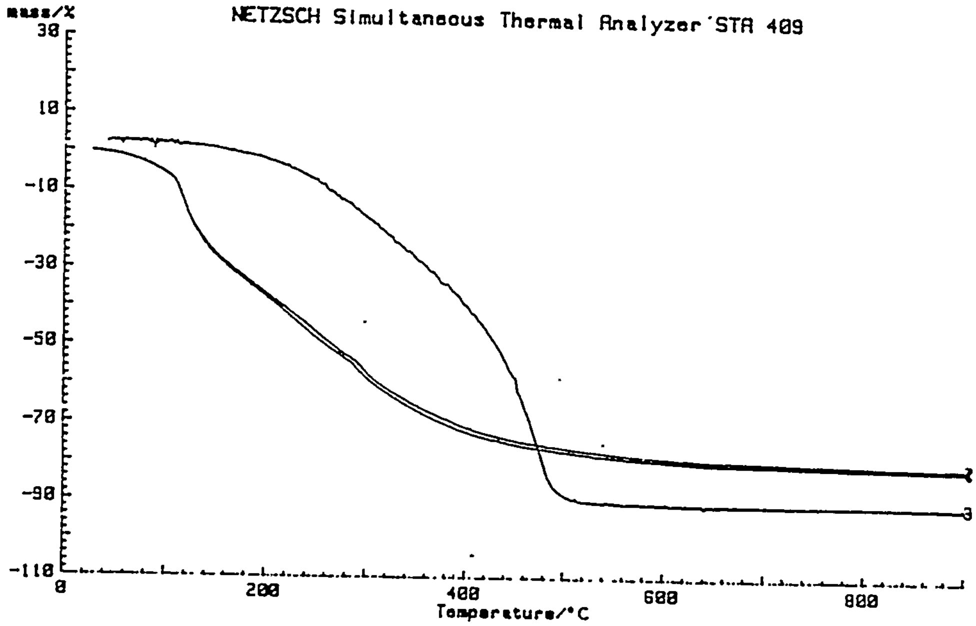

Figure 1. Thermal analysis of bio-oil in inert gas

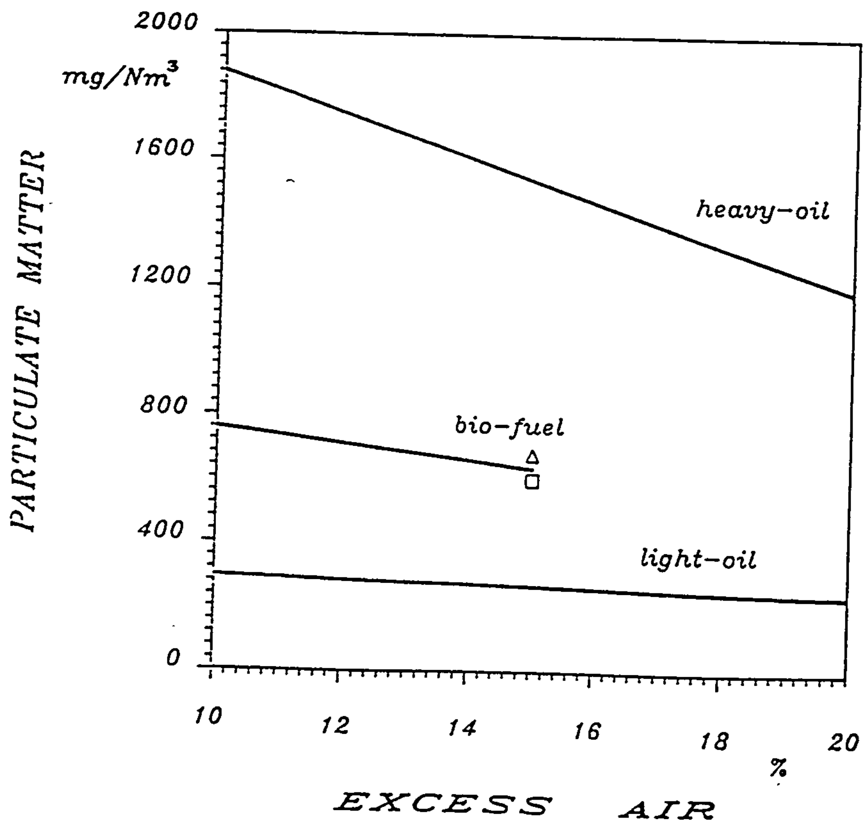

Figure 2. Particulate emission in comparison with traditional fuels

Table 1. Laboratory corrosion test on pyrolytic bio-oil

Corrosion Rate (μm/y)		
Material	25°C	60°C
Fe37	1645	6173
15MO3	1783	5650
T22	1732	3711
T91	678	3830
AISI 304	<0.5	1.9
AISI 316	0.6	<0.5
AISI 321	<0.5	<0.5
AISI 347	2.3	<0.5

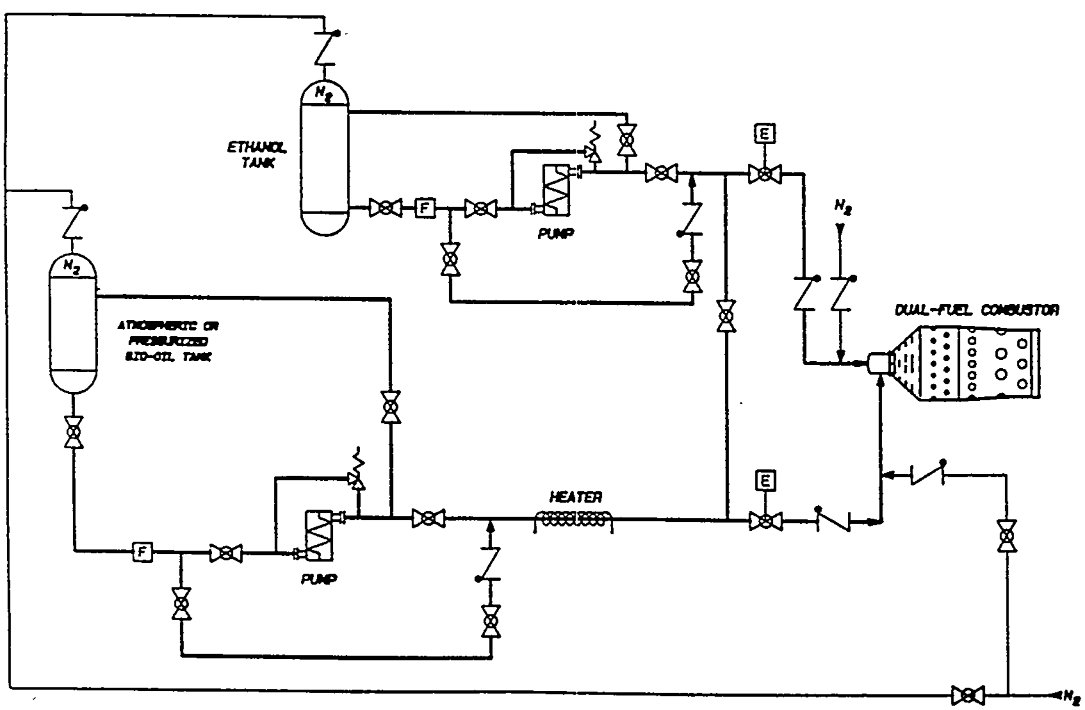

Figure 3. Pressurized test rig for gas turbine combustion tests

ECONOMIC DEVELOPMENT THROUGH BIOMASS SYSTEMS INTEGRATION IN NORTHEASTERN KANSAS

by

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ABSTRACT

In January 1994, the Department of Energy announced that 12 projects were chosen to study the feasibility of integrated production-conversion technologies for energy from biomass systems. The team represented by the authors was chosen for one project reflecting the Midwest region of the United States. The project site is Holton, Kansas (30 miles north of Topeka), a rural community which generates its own peaking power. Based on the results of Phase I and funding availability, some or all of the projects will be selected for demonstration projects.

Dedicated feedstocks for the facility are primarily herbaceous bioenergy crops. To date, the leading candidates are switchgrass, big bluestem/indiangrass, and brome hay. These feedstocks will be supplemented by waste wood from the region. The conversion facility is being designed to convert 100 bone dry tons per day of feedstock into biocrude oil via fast pyrolysis. Process flow diagrams, heat and mass balances and equipment costs are being determined. The oil produced will be shipped to the Holton power plant for electric production. The entire process will produce 3-4 MW of power.

INTRODUCTION

In May 1993, the Department of Energy's National Renewable Energy Laboratory solicited proposals for economic development through integrated biomass systems. The proposals had to include details for the dedicated energy crop to be grown as the source of biomass and the technology used to convert the biomass into electricity or liquid fuels. The Electric Power Research Institute is cofunding the projects which involve electric power generation.

Twenty-four proposals were submitted and twelve were selected for funding. A consortium of groups from the State of Kansas put together a proposal reflecting biomass systems in the Midwest United States. These groups included the Kansas Board of Agriculture, Kansas Electric Utilities

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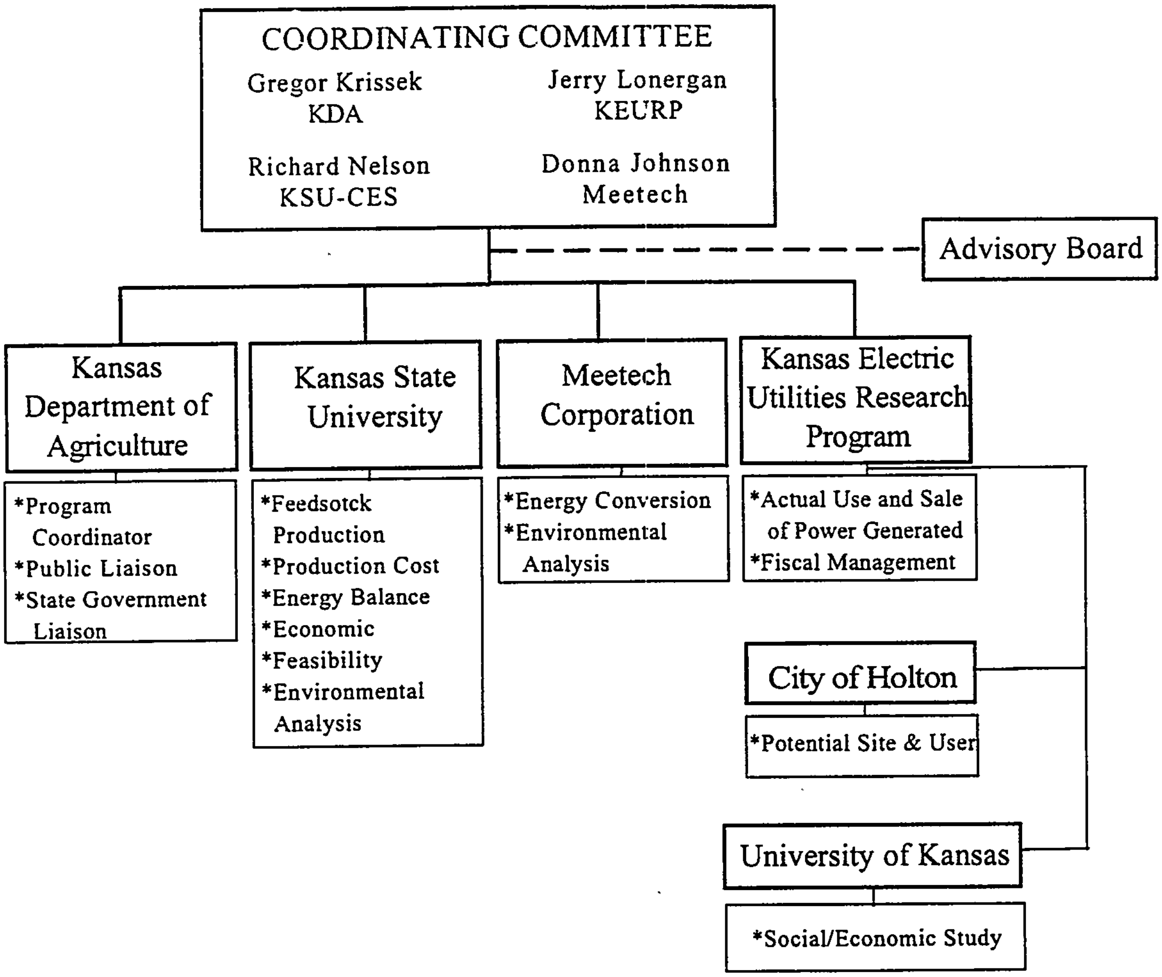


Figure 1. Project Participants and Organization Chart

Research Program, Kansas State University and Meetech. In addition, the City of Holton and the University of Kansas are also involved in the project (see Figure 1). This is a 9 month study and it began in July 1994. This report reflects the first 3 months of work on this project.

SITE SELECTION

The City of Holton, Kansas, was chosen as the site for the facility due to:

1) its reflection of a small but progressive Midwest town with ready access to specialized goods and services available in the Metropolitan Topeka and Kansas City areas,
2) local proximity to feedstocks,
3) a need for a new source of electricity for the future, and
4) a large interest by the City in examining sustainable biomass power production.

Holton is located in northeast Kansas, 28 miles north of Topeka in Jackson County. The community has a stable population base, growing from 3,134 to 3,198 in the 1980's. In 1991, total employment in Jackson County was 4,776 with an unemployment rate of 6.7%. The government is the largest employer and manufacturing employment comprised just under 6% of the total jobs. It is expected that the population will increase with the expansion of the highway between Holton and Kansas and the completion of a major recreational reservoir adjacent to Holton. These two features should continue to enhance Holton as a commuter/bedroom community to Topeka.

Holton currently purchases its base load electricity from KPL, a Western Resources Company. The City, using existing generation capacity, provides for its entire electricity use during peak hours for KPL. When operating, the entire City's electric load is met by the City's generating capacity from 10 a.m. to 10 p.m. Olsson Associates (1992) reported that total annual electricity supplied to the system increased from 27,564.3 megawatt hours (mWH) in 1986 to 33,921.4 mWH in 1991 (just over 23 percent). Using straight line projections based on historical data, Olsson Associates projected total energy requirements of 40,422 mWH by the year 2000. The local generation by Holton in 2000 was estimated at 4,770 mWH (11.8%).

FEEDSTOCKS

Total agricultural land in farms in Jackson County is about 400,000 acres and includes cropland, pasture and trees. Approximately 145,000 acres are in crop production. Crops grown include hay, soybeans, wheat, sorghum, and corn. Land in hay production averaged 50,640 acres from 1980-1991
and land in soybeans and wheat averaged 25,260 and 30,200 acres respectively over the same time period. Average acres for other crops are: corn - 11,320 acres; grain sorghum - 26,000 acres; and sorghum silage - 900 acres.

Dedicated and supplemental feedstocks need to compete with these crops already grown in this area. The bioenergy crops must generate returns that are at least as high as these crops. In this area there are several types of land, those eligible for government farm program payments (payment acres) and land that is ineligible for program payments (non-payment acres). Cash payments are received for producing wheat or feedgrains on payment acres, bioenergy crops will compete more readily on non-payment acres. Approximately 52,200 acres are payment acres in Jackson County.

In addition to these two types of farmland, there is additional land enrolled in the Conservation Reserve Program (CRP). The CRP was authorized by the Food Security Act of 1985 and landowners were paid to take marginal cropland out of production for 10 years. About 21,000 acres are enrolled in the CRP program in Jackson County. Grasses currently grown on these acres include smooth bromegrass, native mixtures, and switchgrass. Restrictions on CRP land use prevent the harvesting of these grasses until after the contracts expire, however, the first CRP contracts expire in 1995.

Nelson et al (1994) have just completed the first assessment of the economic feasibility of growing bioenergy crops in this area compared to conventional crops. They examined conventional crops versus bioenergy crops; payment, non-payment and CRP acres; and low, average and high

productivity soil conditions. In general, they found that bioenergy crops (big bluestem/indiangrass, brome hay, cane hay, eastern gammagrass, fescue, switchgrass) have consistently higher yields than conventional crops (corn, sorghum, wheat, soybeans, alfalfa) regardless of soil conditions. In addition, the total cost per acre is considerably higher for conventional crop production versus bioenergy crop production with the exception of eastern gamagrass. This was due primarily to the fact that bioenergy crops do not have annual seed, planting and field maintenance and that they have lower fertilizer and pesticide costs than conventional crops. When Nelson et al examined average returns of the crops using the relative price relationships projected by the Food and Agricultural Policy Research Institute they found that bioenergy crops can compete with other crops grown in the region. In fact, on low and average productivity soils, only big bluestem/indiangrass, brome hay and switchgrass had positive net returns. In all cases, these three energy crops returned a greater profit to the farmer than conventional crops on both government program and non-program acres. Based on this data, the project will focus on these 3 crops for dedicated feedstocks.

In addition, alfalfa is being examined to determine if it can be used both as an animal feed and as a feedstock for the conversion facility. When used as an animal feed, the producers are trying to maximize nitrogen content in their product. Nitrogen is higher in the leaves and lowest in the stem. Pyrolysis on the other hand requires that nitrogen be minimized. It may be worth separating the leaves and stems of alfalfa. This has the benefits of providing an existing infrastructure, increasing the return for alfalfa pellitizers, and decreasing the nitrogen content for the pyrolysis feed. This approach is being examined by the University of Minnesota.

In addition to using herbaceous energy crops, the project will use waste wood from the area. Based on the projections available to date, we anticipate the approximately 50 bone dry TPD are available in clean wood waste within a 50 mile area of Holton.

CONVERSION TECHNOLOGY

Fast pyrolysis has been shown to convert lignocellulosic biomass into a non-viscous liquid product, with yields up to 75% by weight (Diebold, 1985; Diebold and Scahill, 1988; Graham et al 1988; Piskorz et al, 1988; Bridgwater, 1992; Diebold, 1994) . This material can be used as a fuel oil replacement or as a feedstock for chemicals or upgraded to gasoline. Fast pyrolysis occurs when heat is transferred to biomass with no oxygen present and the solid biomass particles are converted into a mixture of non-condensible gases, water vapor, char particles, and pyrolysis oil vapors. Process temperatures are approximately 500 - 600°C and are maintained by burning the natural gas and/or non-condensible process gases. The residence time of particles in the reactor is less then 2 seconds to minimize the time the pyrolysis vapors are exposed to the high temperatures (thus preventing secondary reactions). After leaving the reactor, the char particles are separated from the hot gas and vapor stream. Next, the vapors are condensed to form a dark brown, non-viscous liquid mixture of organic compounds. The residual non-condensible gases are then recycled to the reactor as motive gas or are burnt to provide process heat (Chum et al, 1989; Bozell and Landucci, 1993; Johnson et al, 1993).

A 100 ton per day (TPD) ablative fast pyrolysis system is being designed to convert the biomass into

biocrude oil. The Holton facility will process both agricultural and wood feedstocks. The system is being designed to handle any combination of the following two streams:

1. 100 bone dry TPD wood biomass with an average moisture content of 50%, or
2. 100 bone dry TPD herbaceous bioenergy crops with an average moisture content of 15%.

Under average operating conditions, the anticipate feed will be 50:50 wood:herbaceous. General flow diagrams and mass balances for 100% wood and 100% herbaceous are located in Figures 2 and 3.

For the Holton facility, Meetech has selected, throughout the process, equipment items which have experienced many years of successful operation in the same or similar application. The exception to this design basis is the fast pyrolysis reactor system. Process design data for the reactor system have been obtained from computer programs of a 1.5 ton per hour pilot plant model by the National Renewable Energy Laboratory (NREL). Design of the computer models is based on several years of laboratory and bench scale reactor studies conducted by NREL.

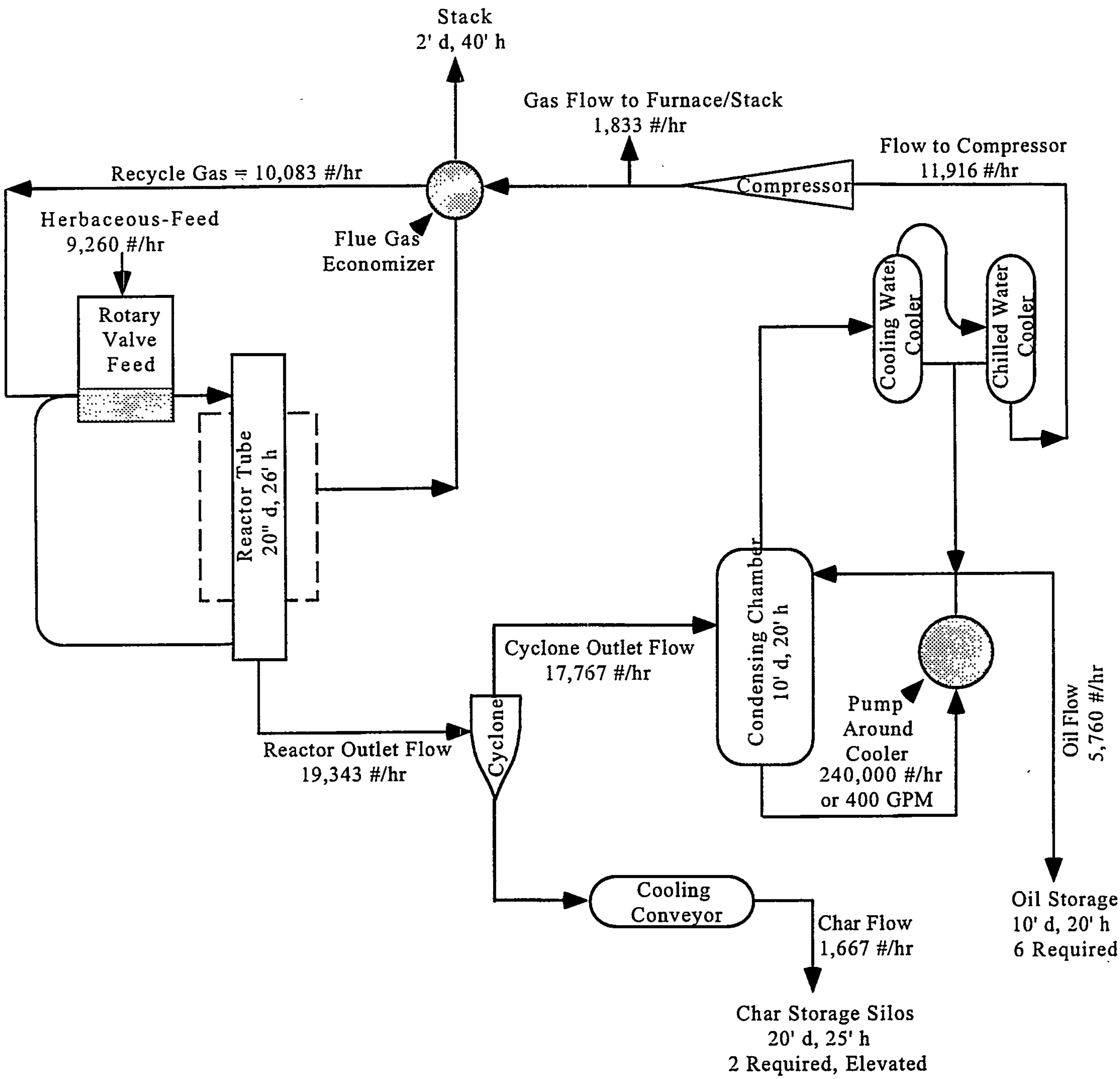
At this time, quotes have been received on most of the major pieces of equipment. It appears the facility will cost between $3.5 - $4.5 million. During the next 4 months the equipment specifications, costs, layout and detailed process schematics will be completed for the system.

One of the major areas of concern during the design phase is the high ash levels associated with herbaceous feedstocks. The ash content of woody fuels is reasonably low, in the range of 0.1-0.5% for hardwoods and 0.5-1.0% for softwoods. Based on a char yield of about 15%, the ash concentration in the char is about 4%. This level of ash does not present problems. Charcoal briquette manufacturers specify a maximum ash in char of 8%, with substantial penalties for higher levels.

However, with herbaceous crops, the ash content generally ranges from 4-10%, thus presenting ash levels in the char of 18-40%. This results in a high ash char co-product and complicates its sale and/or utilization. It may still be possible to manufacture briquettes ourselves. If we slurry the char with the oil for fuel end use, an ash level from wood char is manageable from a slagging viewpoint. However, slurrying herbaceous char in the oil may create serious slagging problems. There may also be problems with burning the char in the furnace as a fuel source.

Table 1 presents different scenarios of wood and herbaceous mixtures to provide a char of 8% based on ash levels in the herbaceous feedstocks of 4, 6 and 8%. In addition, the char from a 50:50 mixture of wood and herbaceous feedstocks is examined. From this table, it can be seen that if more than an 80:20 mixture of wood:herbaceous feedstocks is used, a new market for the char is needed. Part of this project is examining new uses for the char co-product.

Herbaceous Feed



Description

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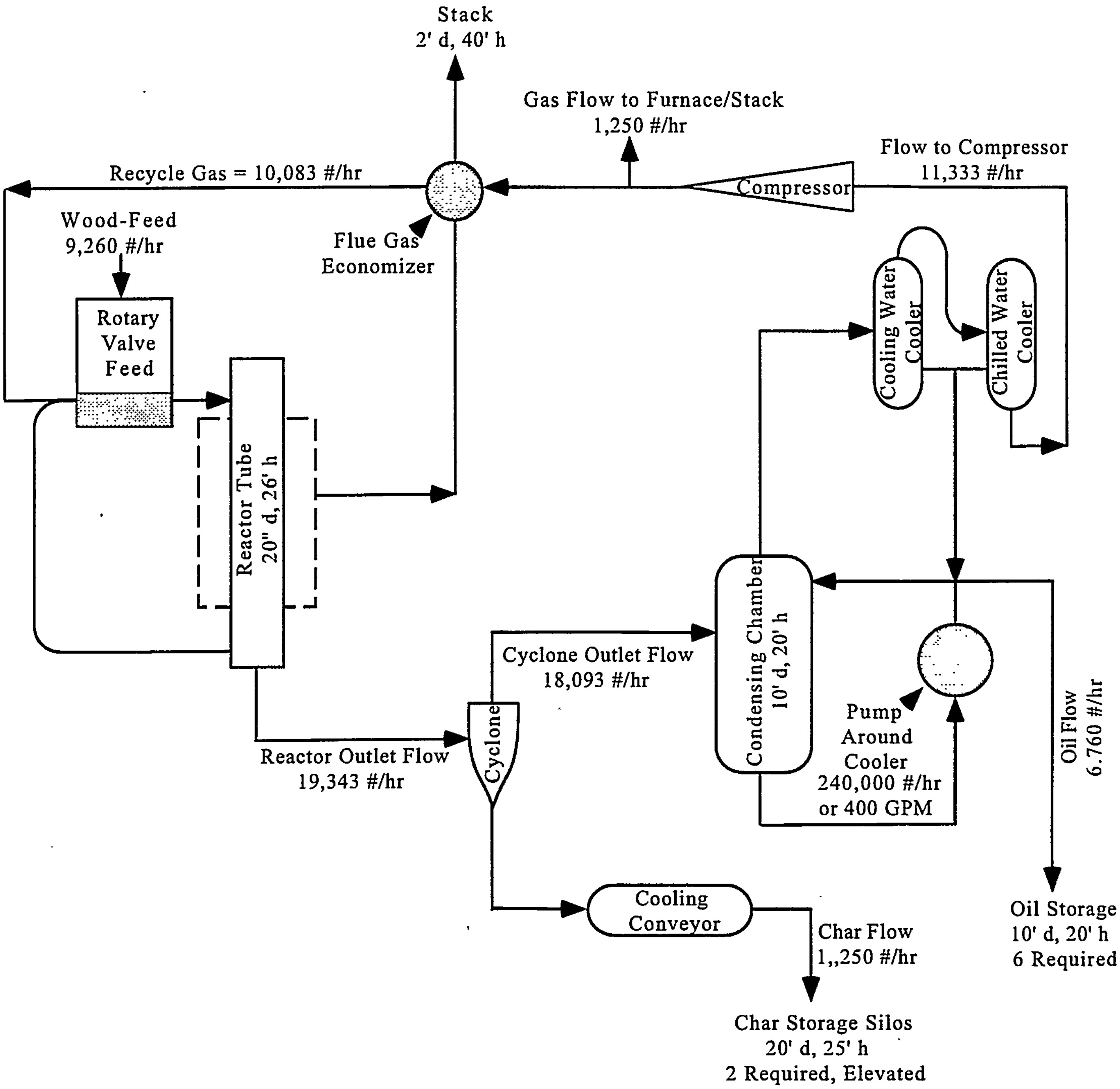
Rev	Date	Description	App.		
				Title: Flow Schematic of Herbaceous Feed	
				Drawn: Mahmoud Asadi	
				Scale: None	Sheet: 1 of 1
				Date: 8/1/94	DWG: 01-01
				App.: Dan Maclean	Rev:

Wood Feed



Description

MEETECH CORPORATION
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Title: Flow Schematic of Wood Feed

Drawn: Mahmoud Asadi

Scale: None | Sheet: 1 of 1

Date: 8/1/94 | DWG: 01-02

Rev | Date | Description | App. | App.: Dan Maclean | Rev:

TABLE 1

MASS BALANCE 100 TPD SYSTEM AT DIFFERENT ASH CONCENTRATIONS

CASE 1

WOOD	ASH CONTENT		ASH CONTENT
	0.6	HERBACEOUS	6
85			
0.15	TPD	15	TPD
12.75	CHAR YIELD	0.22	CHAR YIELD
4	CHAR	3.3	CHAR
	% ASH	27.3	% ASH

BLENDED CHAR PRODUCT FOR CASE 1

0.51	TPD WOOD CHAR ASH
0.9	TPD HERB CHAR ASH
1.41	TOTAL ASH
16.05	TOTAL CHAR
0.09	TOTAL ASH/TOTAL CHAR
8.8	% ASH

CASE 2

	ASH CONTENT		ASH CONTENT
WOOD	0.6	HERBACEOUS	4
80	TPD	20	TPD
0.15	CHAR YIELD	0.22	CHAR YIELD
12	CHAR	4.4	CHAR
4	% ASH	18.2	% ASH

BLENDED CHAR PRODUCT FOR CASE 2

0.48	TPD WOOD CHAR ASH
0.8	TPD HERB CHAR
1.28	TOTAL ASH
16.4	TOTAL CHAR
0.08	TOTAL ASH/TOTAL CHAR
7.8	% ASH

CASE 3

WOOD	ASH CONTENT		ASH CONTENT
	0.6	HERBACEOUS	8
90			
0.15	TPD	10	TPD
13.5	CHAR YIELD	0.22	CHAR YIELD
4	CHAR	2.2	CHAR
	% ASH	36.4	% ASH

BLENDED CHAR PRODUCT FOR CASE 3

0.54	TPD WOOD CHAR
0.8	TPD HERB CHAR
1.34	TOTAL ASH
15.7	TOTAL CHAR
0.09	TOTAL ASH/TOTAL CHAR
8.5	% ASH

CASE 4

	ASH CONTENT		ASH CONTENT
WOOD	0.6	HERBACEOUS	6
50	TPD	50	TPD
0.15	CHAR YIELD	0.22	CHAR YIELD
7.5	CHAR	11	CHAR
4	% ASH	27.3	% ASH

BLENDED CHAR PRODUCT FOR CASE 4

0.3	TPD WOOD CHAR
3	TPD HERB CHAR
3.3	TOTAL ASH
18.5	TOTAL CHAR
0.18	TOTAL ASH/TOTAL CHAR
17.8	% ASH

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INTEGRATION OF BIO-OILS INTO UTILITIES INTRODUCING NEW RENEWABLE TECHNOLOGIES

by

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ABSTRACT

The Kansas Electric Utilities Research Program (KEURP) is a cooperative venture of seven member electric utilities which operate in the State of Kansas. The goal is to "perform research to proactively seek and deliver technologies enhancing the value of electric services to its members, utility customers, and the State of Kansas." KEURP program activities are guided by two working committees.

During 1994, KEURP developed a renewable energy and development research plan. A goal of this effort was to identify the most effective Kansas renewable resource(s) that, short term have the potential to be economically viable. A second activity, associated with the Biomass Pyrolysis Oil Combustion Workshop has been to discuss with members of the Executive Committee the processes involved with decisions to bring new technologies into an individual utility. Ideas presented should not be interpreted to represent the belief or policy of any individual member of KEURP or a policy of KEURP. The information is a collective interpretation, by the author, of informal conversations and comments and opinions expressed on an individual basis by Executive and in some cases Technical Committee members.

Risks are not easy to defend or justify in the current electric utility environment. As long as expectations are for long-term accountability for decisions made by utility companies; inventors, scientists, and advocates of various renewable sources (or other emerging technologies) should expect to be tasked with being able to demonstrate the effectiveness and economics of individual technologies. For new ideas/methods to become a part of a utility's operation, the driving factor has to be the economics of a project. The sometimes sizeable obstacles of locating funding support for basic and demonstration research will be impacted even more so as competition grows among the utilities. Funding support for and eventual adoption of new, and riskier, technologies are even less likely without effective demonstration projects.

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INTRODUCTION

This paper presents a very general assessment of the interest and perspective of a set of Kansas utilities in renewable energy research and potential for adopting new renewable energy technologies. The work is not intended to provide a conclusive answer to the interest of utility executives in biofuels as a source for electric generation. It is merely an overview of planning efforts and interviews regarding the broad category of renewable energy in Kansas. No conclusions are drawn and no direct attribution to a Kansas utility representative is included in this paper. Suggestions and ideas generated from this paper are those of the author based on his interpretation of comments and responses to questions posed during research on renewable energy in Kansas and in-person interviews.

The paper is presented to serve as a tool for developers, inventors, and advocates of various renewable technologies to help them understand challenges and opportunities that exist. The paper reviews two efforts undertaken by the Kansas Electric Utilities Research Program during 1994 to develop a better understanding of and a plan for renewable energy research in the state.

KANSAS ELECTRIC UTILITIES RESEARCH PROGRAM (KEURP)

KEURP was formed in 1981 by six investor owned utilities operating in Kansas. Mergers, utility business decisions, and new membership have resulted in a total of seven member utilities now belonging. These utility members are: The Empire District Electric Company; KG&E, A Western Resources Company; KPL, A Western Resources Company; Kansas City Power & Light Company; Midwest Energy, Inc.; Sunflower Electric Power Corporation; and, WestPlains Energy.

The organization is funded by an assessment based on the local research portion of membership fees paid to the Electric Power Research Institute (EPRI). The Executive Committee in 1993 developed this mission: KEURP will be a cooperative venture performing applied research to proactively seek and deliver technologies enhancing the value of electric services to its members, utility customers and the state of Kansas.

The main components of KEURP's structure are: 1) Executive Committee - The Executive Committee functions much like a Board of Directors. Its members are the president/chief executive officer, or designee, of the seven member utilities, the chair of the Kansas Corporation Commission (KCC, the state's utility regulatory body), and a representative from the Kansas Board of Regents. The committee directs the organization's efforts to achieve its goals, approves the annual research agenda developed by staff and the Technical Committee, and oversees the successful completion of individual research projects.

2) Technical Committee - Each member utility and Board of Regents institution appoints one person to serve on the KEURP Technical Committee. The KCC also designates one person to serve as a liaison to KEURP, usually the Chief Engineer. The Committee meets every two months to review on-going research, consider any submitted proposals, and discuss future research opportunities. If funding the proposal is not recommended by the Technical Committee it is returned to the investigator, recommendations to accept a proposal for KEURP funding are forwarded to the Executive Committee for its discussion and vote.

KEURP creates advisory groups on specified research topics. These groups are comprised of people, not necessarily on the Technical Committee, having a particular subject expertise.

KANSAS RENEWABLE ENERGY RESEARCH AND DEVELOPMENT PLAN

During 1994, KEURP developed a renewable energy research and development plan. The final report included a list of research work that could be conducted through 1997 and will provide information to allow utility companies to make decisions regarding future use of renewable energy. There were a number of "assessment tasks" identified in the plan. These tasks included:

1) wind data collection at potential wind farm sites in Kansas;

2) initiate an education effort for utility professionals concerning off-grid photovoltaic opportunities;

3) continue participation in a feasibility study of biomass electric generation in northeast Kansas; and,

4) assess the interest of Kansas utility customers in supporting, through their monthly electric bill, specific renewable research/demonstrations.

A review of this list reveals a conservative approach to renewable energy development with a focus on data collection, education and assessments. There is no anticipation of large scale renewable energy projects. This was a project that involved a review of existing renewable technologies, advances made and short-term anticipated enhancements to the renewable energy technology base, and some consideration of existing/future capacity requirements. The end result can be summed as a good research program with a focus of careful evaluation. This program is unique to Kansas, if other groups of utilities conducted a similar research effort their's may be a more aggressive "building" type research program. However, for Kansas and a set of seven utilities the plan appears to suggest the need for more information, short term, before building, demonstrations projects or new technologies are developed.

EXECUTIVE COMMITTEE INTERVIEWS

As part of an annual process to evaluate the performance of KEURP and begin to develop the following year's research agenda interviews are held with all participants in KEURP. In-person visits at each utility and university are held. In prior years there had been the, almost unanimous, recognition that it was important to "do something" on renewable energy. More difficult had been the task to specifically identify what that "something" was. To better define the renewable research effort, the plan referenced above was developed. As part of a follow-up to the planning conducted, interviews this year probed in more detail what are key components of renewable technologies to identify future research opportunities.

Presented below is a very general overview of comments shared during more then 30 interviews. The interpretation given these ideas are the authors. No idea presented below is by itself the belief of one person or one company.

The critical variable in adopting new technologies is the economics of any type of renewable project. If a project can not stand on its merits, the project will not be done. As competition moves forward in the electric utility industry, projects will be subjected even more so to testing feasibility and appropriateness. While in the past there existed some ability to conduct demonstration projects, that flexibility is quickly eroding. Decisions will, at least for now in the short-term, be based on the projects ability to deliver electricity at the lowest cost, utilities are becoming even more risk-adverse then in the past. New technologies will probably have to be developed by independent power producers, and/or depending on the quality of a project, spin-off for profit subsidiaries of the utility companies may be a capital source.

Increasingly, the Federal government will be viewed as a primary source for demonstrations/ventures of risky new technologies and basic research. This is a source with a limited amount of flexibility to identify and participate in more basic type research and prototype development. State governments can provide support, depending upon the maturity and creativity of its economic development infrastructure. Kansas, for example, with the Kansas Technology Enterprise Corporation provides match support, on a competitive basis, for some basic and applied research that can chow potential for eventual commercialization. Another example is the state's creation of tax credits/incentives for individual investors in state-approved venture capital funds.

The utility industry in the past has provided a significant base of support for research. But, as deregulation and competition becomes inevitable this research support, particularly cooperative projects, will be more difficult to defend and justify. A key to funding will be to demonstrate the economic value of proposed technologies.

To some extent, research entities like KEURP or EPRI may also be a source for funding. However, an organization's mission may dictate their interest and willingness to support various projects. For example, KEURP's research is increasingly being tasked with demonstrating the bottom line impact of research it funds. How will an investment in a specific project improve êlectric generation in Kansas? Additionally, KEURP has a specific mandate to not fund basic research - the fine line between basic and applied research is, and more so in the future will be, a constant source of discussion in reviewing proposals.

Research has always been a poor step-child to the nation's economic and technological development. While academic and industrial organizations voice strong support for research as critical to the country's future, funding to support research has been another matter. Inventors and entrepreneurs in the United States have always weathered this lack of research funds. While a very positive and rallying point has been the ingenuity and creativity of these people in finding a way to bring their technology to commercialization, the fact is pushing technologies from ideas to the shop floor has never been easy and will continue to be even more of a challenge in an era of competition.

Comparative Study of Various Physical and Chemical Aspects of Pyrolysis Bio-Oils Versus Conventional Fuels, Regarding their use in Engines

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Abstract

The objective is to present a comparative study of the physical and chemical characteristics of the bio-oils versus conventional fuels like petrol, fuel-oil, etc. From consideration of the bio-oil characteristics which most influence its use in engines (density, viscosity, water content, solubility, ash percentage, C, H, O %, HHV) a prediction of the performance of engines (alternatives and turbines) fueled with this product will be made. The most adequate types of engines will be discussed. Different alternatives to overcome the problems, and required modifications in engines, will be researched prior to bio-oil utilization at industrial scale.

1.- Introduction

The bio-oil resulting from the pyrolysis of vegetable products, at an intermediate oxidation state, can react with oxygen in a combustion process. The liquid products obtained from the pyrolysis of wood, and more specifically those derived from fast pyrolysis, are mainly a mixture of aromatic and linear hydrocarbons, alcohols, aldehydes, phenols, water and other products resulting from the feedstock used (lignin, sugars, etc.). Therefore its oxidation reaction is possible with the oxygen in the air (Bridgewater, et al., 1991). Its composition varies according to the raw materials from which it was obtained and the specific conditions of the pyrolysis process, therefore it is only possible to speak about the average characteristics of the pyrolysis product. To label a substance as "fuel" it must fulfill a set of characteristics in relation to combustion and the elements capable of producing and maintaining it; i.e. it must be standardized. A main objective is, therefore, to reach this state for the pyrolysis bio-oils.

Let us pretend that the so called state of "fuel" for these products has been reached. Then it can be burned in a reciprocating internal combustion engine. In the case of a compression-ignition engine (diesel), the combustion of the fuel injected at a high pressure into a chamber of air preheated by the compression, is developed. The ignition is caused by self-ignition of the fuel and the combustion occurs at an almost constant volume.

If the low volatility of the bio-oil restrains its premixture with air during the injection process, then the bio-oil must be injected at high pressure into the chamber, but the bad ignition quality may force the ignition to be promoted. This paper is centered on the utilization of bio-oils in diesel or dual fuel engines, although most of the conclusions can be applied to other types of engines. The combustion in a diesel engine is considered to begin when the fuel injection into the chamber starts at the end of the compression, and when the air is already at a high temperature. The combustion takes place basically in three phases as shown on figure 1: delay period, fast combustion phase, and final phase. The second phase is strongly influenced by the amount of fuel injected during the delay period, the conditions of the mixture, and the evaporation of the fuel in this period. The evaporation is in relation to the characteristics of the injection jet and the movement of air in the chamber.

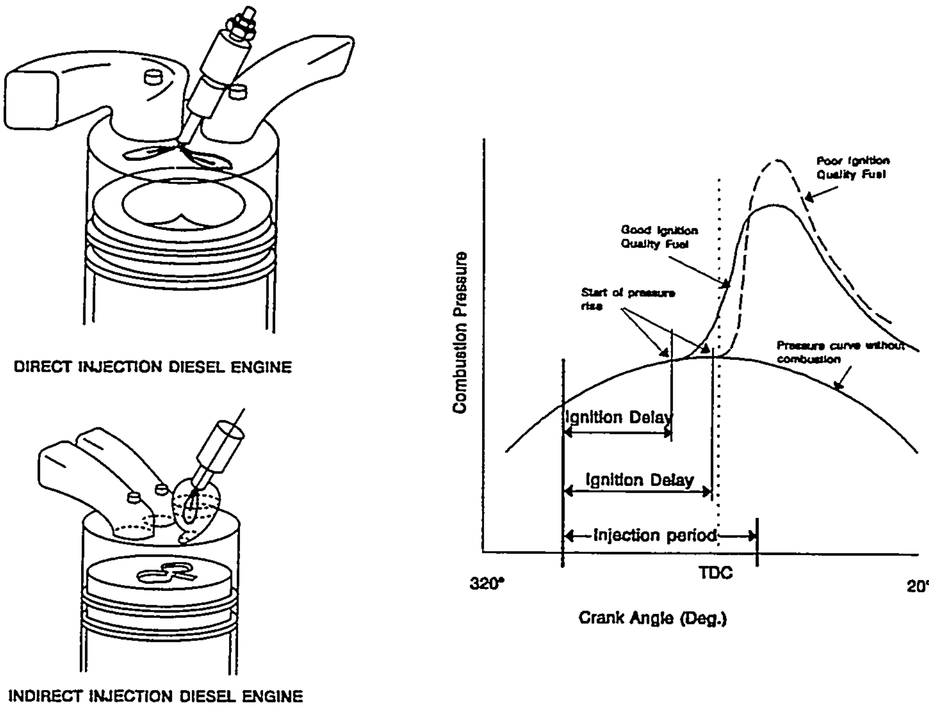

Fig. 1.- Diesel engine. Combustion chamber and pressure diagram.

TABLE I.- Diesel fuel specifications in Spain

Property	Units	Diesel oil	Fuel oil Nº1	Fuel oil Nº2
Density (15°C) Max Min	kg/dm³	 0.860 0.825	 - -	 - -
Sulphur max.	% by mass	0.30	2.70	3.50
Cetane Index	–	45	–	–
Distillation 65% 85% final	 °C °C °C	 250 350 380	-	-
Kinematic viscosity Winter (max.) Summer (max.)	 mm²/s mm²/s	(40°C) 4.3 5.2	(100°C) 25 25	(100°C) 37 37
Flash point (min.)	°C	55	65	65
Carbon residue (Ramsbotton) max. on 10%	% by mass	0.2	-	-
Water and sediments	% by volume	0.1	1	1
High Heating Value (min.)	MJ/kg	43.96	42.29	41.45
Low Heating Value (min.)	MJ/kg	–	40.19	39.36

The composition of conventional diesel oils, gas-oils or fuel-oils varies hugely according to the origin of the and the refining process, but it is basically a mixture of hydrocarbon chains made up of 16 to 34 carbons. These chains are aromatic and more or less branched. The composition of these fuels must meet minimal specifications such as the ones shown in Table I for the fuel in Spain. To these minimal specifications the producers add some others, among which the following can be pinpointed: lubricity, detergency stability and corrosivity.

Taking into consideration the main common characteristics of bio-oil, the following options can be considered for its use in compression-ignition engines (diesel): (a) Conventional diesel engine with minimal modifications as far as materials and adjustments of the injection system, (b) Multifuel diesel engine such as those designed for military applications with preinjection and special injection equipment and combustion chambers, (c) Specially designed engines for this type of fuel, such as the example of the Esbeltt engine designed to use vegetable oils (oxygenated and high viscosity), which would be a starting point for this case, and other high turbulence pre-chamber type engines. The combustion chamber would be redesigned to make it more compact, the injection system would probably have a double injector and the materials would be stainless, and finally, (d) A dual fuel re-designed engine in which another fuel promotes the ignition of the bio-oil (like the work presented by the VTT), or a stratified chamber with a volatile fuel premixed with air and spark ignited.

2.- Characteristics of a Pyrolysis bio-oil.

The characteristics of a pyrolysis bio-oil that most determine its performance regarding combustion are compared with the conventional Diesel fuels.

2.1.- Acidity. Since it is impossible to increase the low pH (2,0 to 2,4) in these bio-oils, the conventional steels that comprise a large part of the materials in contact with the fuel must be substituted by steel resistant to corrosion or other materials. Stainless steels are being studied bearing in mind some problems such as the machinability, hardness, malleability, etc.

2.2.- Stability. The proven fact that the bio-oil changes its properties with time, mainly viscosity and composition, is a problem that can be solved by means of using the fuel promptly. We have seen this problem intensified in tanks subjected to the high summer temperatures of Madrid. We have also seen that the injection system parts, using this fuel, are totally jammed and stuck after 24 hours (without functioning) if the bio-oil has not been cleaned after stopping the engine.

2.3.- Decomposition. At a temperature of greater than 100°C, the bio-oil starts a quick decomposition process that leaves it totally useless. This is another important difficulty since it is very likely that in particular parts of the injection system and the spray, the bio-oil is subjected to high temperatures before starting the combustion. If the injection is done in the chamber, and the combustion does not take place or is done under bad conditions, the interior is coated with a dark brown, easily detached, solid. In the same way, in the areas near the injector nozzle, some amount of liquid fuel settles where, being subjected to high temperatures, it polymerizes and oxidizes. This can be avoided by designing auto-cleaning injectors or avoiding liquid in these areas.

2.4.- Water content. The water content of a conventional fuel is very low, though at an experimental level diesel fuel emulsions with up to 15% water, with an emulsifier, have been used in order to reduce the combustion temperatures and therefore the NOx emissions. Nevertheless the

water content near 20% produces ignition difficulty and reduction of the fuel heating value. The water takes part of the energy of combustion.

2.5.- Oxygen content. Although the chemical composition of the fast pyrolysis bio-oils is not yet very well-known, the information we have tells us that it is a mixture of oxygenated organic products. This produces a low heating value of 16 MJ/kg compared to the 42 MJ/kg of a distillated diesel fuel. The water requires, for its evaporation, around 3% or 4% of the liberated heat during combustion. Taking the example of the product of eucalyptus chips flash pyrolysis with 44.2% of C, 7.1 of H and 47.5 of O, a stoichiometric relation results with 10.5 kg air/kg bio-oil. This relation is 14.5 for conventional gas-oils and fuel-oils, 6.4 for methanol and 9 for pure ethanol.

3.- Bio-oils in Diesel Engines

The specific problems in the use of fast pyrolysis bio-oils in diesel engines are highly related to the general combustion characteristics previously mentioned, together with those related to their physical properties and performance in the autoignition and specific conditions of the combustion in this type of engine.

3.1.- Density. The typical density of some studied bio-oils at 15°C ranges from 1.20 to 1.27 kg/dm^3 compared to the 0.83 - 0.85 kg/dm^3 of the distillates diesel fuels and 0.97 to 0.99 kg/dm^3 of the heavy fuel oils. This has several consequences. The injection system control of a diesel engine is volumetric, therefore the injected mass per piston stroke can be larger; this is not so important if the injection system is completely re-designed. On the other hand, the characteristics of an injection jet are strongly related to the Reynolds and Weber number of the flow process. These are functions of the injected-fluid density. This parameter must be considered in the study of the injection system performance with a bio-oil or in its re-design.

3.2. Viscosity. In the study of fuels the kinematic viscosity is normally used. This is an important parameter in the performance of diesel engine injection systems. Viscosity affects greatly the characteristics of the injected jet, figure 2, and the lubrication of the injection-system internal elements, figure 3. From the literature review and the measurements that we have made, a variability in the kinematic viscosity of the different samples was observed. The values at 50°C range from 7 cSt to 121 cSt.

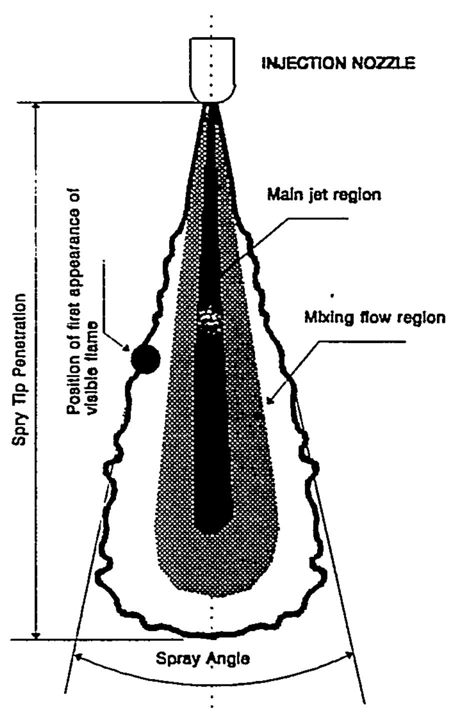

Fig. 2.- Typical Diesel spray

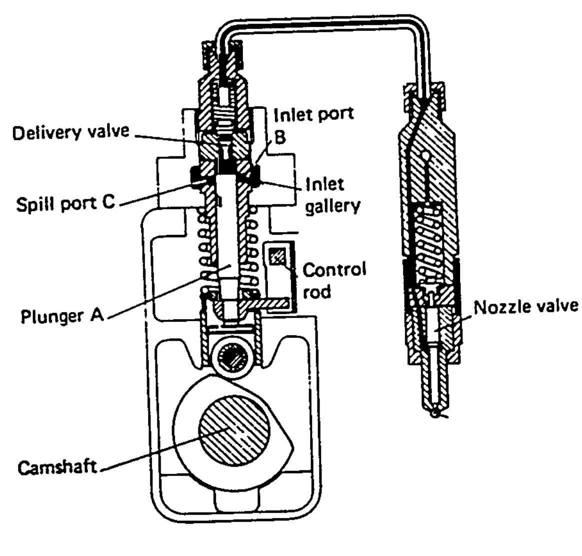

Fig. 3.- Typical Diesel injection system

The viscosity of the bio-oil is an important function of its water contents, therefore the low viscosity samples that we have handled were normally of high water-content bio-oil. A possible way of reducing the viscosity is by adding ethanol or methanol, although the ignition characteristics of the bio-oil are then worsened. It is then necessary to add ignition promoters. Figure 5 shows the viscosity in relation to the temperature for different mixed methanol proportions.

3.3.- Surface tension. This parameter is relevant to the injection spray formation and the size of the droplets. Its value is reduced as the temperature is increased. Figure 6 shows the surface tension of different fuels compared to one known value for a bio-oil. The observed differences are not big enough to expect great differences as far as the performance is concerned.

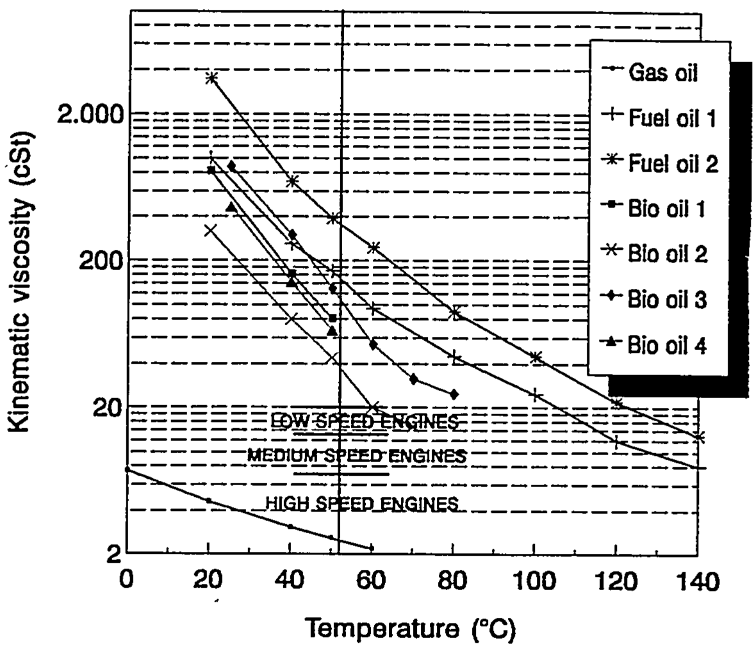

Fig. 4.- Viscosity - Temperature for various fuels

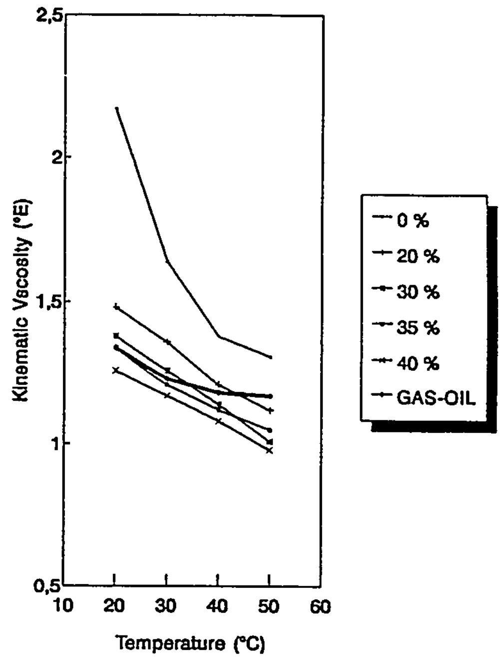

Fig. 5.- Kinematic Viscosity of bio-oil - methanol mixtures

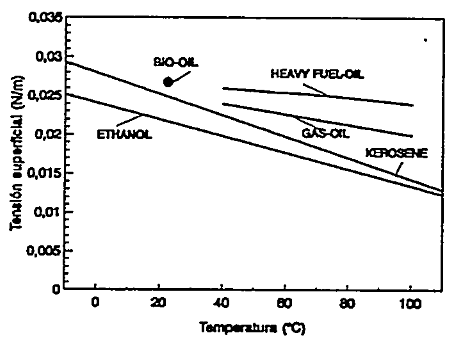

Fig. 6.- Surface Tension for various fuels

3.4.- Cetane Number. The Cetane Number is a measurement of the characteristics of a fuel as far as the ignition in a diesel engine is concerned (Owen, 1990). High Cetane Numbers are associated with linear and long chain hydrocarbon fuels (16-30 carbon atoms) whereas, low numbers are related to aromatic and short chain hydrocarbon fuels. Cetane is measured in a standardized test using a laboratory CFR diesel engine. The Cetane Index is a number obtained from some characteristics of the fuel after an equation of the type (ASTM Standards):

$$\textit{Cetane Index} = 454.74 - 1641.416\,D + 774$$

where D is the density at 15°C and 50% recovery temperature in the volatility curve (corrected to standard barometric pressure) and it correlates well to the Cetane Number for petroleum derived fuels. More sophisticated equation are used in the ASTM D 4337. Other studies estimate the Cetane Number from carbon type and structural composition of a petroleum fuel (Glaavincevski, 1984). Applying with reserve the simple equation to a typical bio-oil, the obtained values range from 47 to 50, which is in contrast with the proved bad ignition quality of the bio-oil (Solantausta, et al. 1993). Common values are 45 to 50 for automotive diesel oil and 20 to 35 for heavy fuel-oil, which shows that the above equation is not useful for other than petroleum fuels. Probably, it will not be feasible to measure the Cetane Number in a conventional CFR Engine, since it has been standardized for conventional petroleum fuels.

A high Cetane Number indicates a low "delay period" in the diesel engine combustion and vice-versa. The delay period, which is really the first combustion phase in a diesel engine (Baert, 1990), according to figure 1, is the period during which the chemical, non-exothermic reactions take place before the premixed or rapid combustion phase. This is prior to the fast heat release of the second phase. Therefore, high delay periods are associated with short second combustion phases and generally high pressure gradients in the chamber. Very high delay periods, such as the ones that would be obtained with light hydrocarbons (gasolines), would cause ignition problems since the second phase would be delayed with a cold engine. The typical composition of some of the studied bio-oils show aromatic hydrocarbons and short chain organic products (less than 8 to 10 Carbon atoms) so the characteristics in diesel engine combustion should be quite poor, and a Cetane improver must be added and another combustion technique with pilot injection, double injection, simultaneous injection of gas-oil, or fumigation with ether or another volatile fuel must be used.

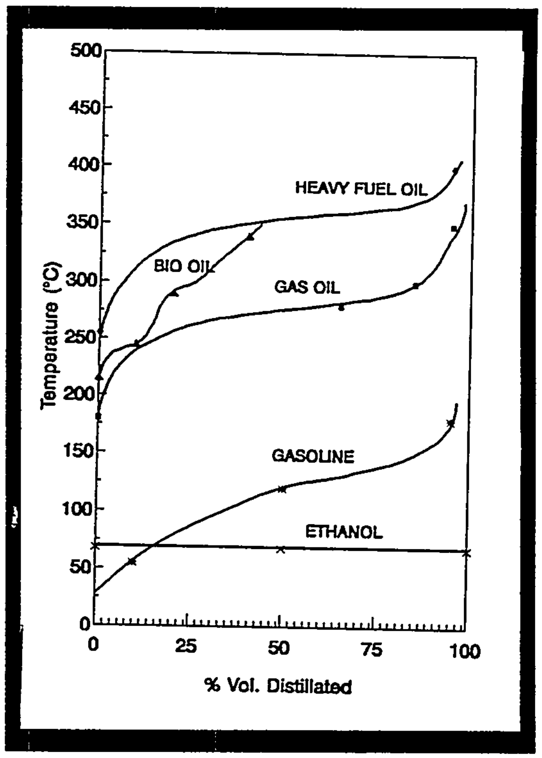

Fig. 7.- Distillation curves of various fuels

3.5.- Carbon Residue. This parameter indicates the tendency of a fuel to form coke deposits. In the case of diesel engines it is related to the combustion of fuel droplets and soot formation. The air temperature evaporates first the volatile components of the atomized spray drops and the temperature increase caused by the combustion tends to crack the final part of the droplet. The

Conradsson (ASTM D 189) or the Ramsbottom (ASTM D524) methods are usually employed. The available data on this parameter for bio-oil are contradictory. The composition of a bio-oil is made up of aromatic rings, but with a low carbon number, which gives opposite tendencies to this parameter. Therefore, this parameter is affected by the composition of a particular bio-oil, according to its feedstock material.

3.6.- Heating Value. Less maximum power for a given engine displacement is a direct consequence of the lower heating value of bio-oil in comparison to conventional diesel fuels. Nevertheless, due to a lower stoichiometric relation, it is reasonable to expect that a greater mass of bio-oil can be injected for each unit of air mass than with diesel fuels, while at the same time keeping the particle emission level constant.

3.7.- Volatility. The volatility of a Diesel fuel measures the evaporation capacity in the combustion chamber. It is expressed as a function of the temperature at which successive fractions distill under standardized test conditions. Volatility effects the smoke emission, but it is also related to other characteristics such as viscosity, density, and Cetane Number. Figure 7 shows the typical distillation curve for two diesel fuels and a studied bio-oil. The fast decomposition when reaching temperatures around 140°C impedes making the complete test for the bio-oil. The knowledge of this curve is useful to predict the droplet evaporation time and its combustion, both factors affect the coking of the injection nozzles and soot emission.

4.- Comparative study of a diesel engine with a bio-oil and a conventional diesel oil.

Problems related to combustion and the use of bio-oils, such as acidity, stability, decomposition at a particular temperature, and ignition difficulties, are not taken into account; only some comparative tendencies between the estimated performance of conventional diesel fuels and diesel engines working on bio-oil are considered.

4.1.- Injection system performance. The injection jet in a diesel engine combustion chamber develops at the so called "atomization speed" (Gupta, 1985). The initial speed of the injected spray into the chamber is around 100 m/s, spreading and mixing with the surrounding air, and breaking up into thin drops of about 10 µm around the nozzle. The air mass affected by the spray increases as it goes away from the nozzle, it also increases its width, and its speed decreases due to aerodynamic effects. Fuel droplets (10 µm to 150 µm) evaporate absorbing heat from their environment, and the spray keeps penetrating in the chamber. The spray is made up of various areas as it is shown by figure 2. The droplets at the periphery of the spray are the ones which first entered into the chamber, and therefore the first ones to release energy. The development of the spray and its interrelation with the combustion is studied by three parameters: spray angle, penetration, and average drop diameter (Henein, 1990).

A criterion to establish the atomization speed at the nozzle outlet is that $(\rho_l/\rho_g)^{1/2}$ has to be smaller than a constant k dependent from the nozzle geometry (usual values range from 6 to 12) (Heywood, 1988). For sprays in the atomization speed, the spray angle can be estimated by the relation (Kuo, 1982):

$$\tan(\theta/2)=\frac{2}{3A}\pi\,(3\rho_g/\rho_l)^{1/2}$$

where ρ_g and ρ_l are the gas and liquid densities and *A* is a constant which depends of the nozzle geometry.

To estimate the spray tip penetration the following relation can be used (Henein, 1972):

$$S=const\,\Delta p^{0.22}\,\rho_g^{-0.14}\,\rho_f^{0.23}\,\sigma_f^{-0.28}\,t^{1/2}$$

Where Δp is the pressure drop at the injection nozzle, *t* is the time since the beginning of the ignition.

Although the fuel distribution in the chamber is important, the atomization of the spray into small droplets is also basic to increasing the contact area with the air. During the period in which the injection takes place, the conditions affecting the spray formation vary, so the distribution of drop sizes varies with time and the position in the spray. The aerodynamic theory of sprays in atomization regime predicts that the average drop diameter can be expressed by the relation:

$$D_{dm}=const\,\frac{2\pi\,\sigma_f}{\rho_g v_r^2}$$

in which σ is the surface stress and v_r is the injection average speed which is a function of the pressure drop at the nozzle.

TABLE II.- Diesel injection parameters

Parameter	Gas-oil (50°C) (Typical)	Fuel oil (100°C) (Typical)	Bio oil (50°C) (Typical)
θ	15° - 20°	13° - 19°	12° - 17°
Re/Re^*	1	0.14	0.02 - 0.06
We/We^*	1	0.6	0.7
ρ_l/ρ_l^*	1	1.18	1.40 - 1.45
ν/ν^*	1	8	20 - 55
σ/σ^*	1	1.8	1,5
D_d/D_d^*	1	2.12	2.2
S/S^*	1	0.88	0.94

$Re = d_n\,v_j / \nu_l$ $We = \rho_l\,v_j^2\,d_n / \sigma$ d_n: injection nozzle diameter *: Gas-oil

Table II shows the results of the characteristic parameters of the injection spray for a gas-oil, a fuel-oil (preheated to reduce its viscosity) and a typical bio-oil. The observed differences are in some cases great enough to predict important differences in the injection system performance, specially troubles in the correct formation of the injection spray. The main parameter to reduce

is viscosity, since other parameters such as density and surface tension do not present significant differences. Figure 8 shows the results of the injection tests carried out with a mixture of bio-oil and methanol compared to those of automotive diesel oil. In this case the performance differences are not very significant because of the viscosity adjustment, but are according to the predicted theory.

4.2.- Specific Power. The effective specific power of a diesel engine can be estimated as follows:

$$Pe = V_f \rho_f LHV \eta_i \eta_m / V_T$$

Pe: Specific Output
V_f: Injected fuel flow
ρ_f: Fuel Density
LHV: Low heating value of the fuel
η_i: Indicated efficiency obtained from the p - V diagram
η_m: Mechanical efficiency
V_T: Displacement

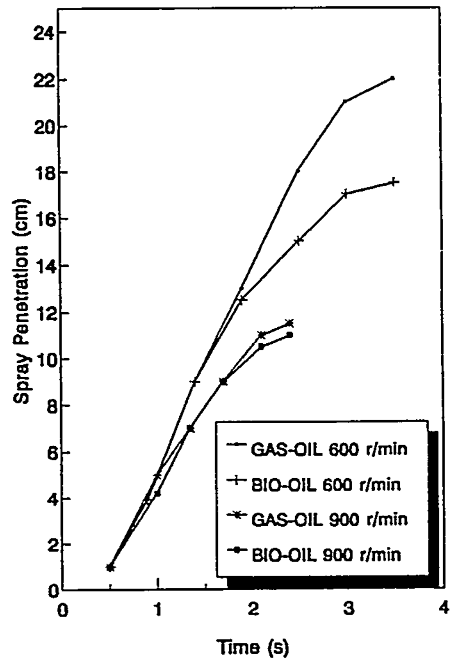

Fig. 8.- Injection spray tip penetration for bio-oil and gas-oil

It could be assumed that the indicated efficiency of the engine is reduced 10% at full power because of the increased difficulties in burning the bio-oil. Assuming the same volumetric efficiency, rotational speed, and mechanical losses for the diesel engine, and assuming that the amount of fule injected can be increased in the same proportion as the stoichiometric ratio without increasing combustion problems and soot emissions, the specific maximum power P_e of the engine with bio-oil (feedstock: Eucalyptus chips, composition %C: 44,14; %H: 7,1; %O: 47,6; H_2O: 22%) could be estimated in relation to a Diesel fuel:

$$P_e \text{ (bio-oil)} = (0.85 - 0.89) \cdot P_e\text{(Diesel fuel)}$$

These approximate values can be modified with the engine functioning by an improvement in the combustion systems or when acquiring experience on the engine power limits. In a diesel engine operating the maximum power is mainly fixed according to some of the following factors: thermal tensions, mechanical stresses, factor of utilization, application and the legal limits of smoke emission.

Changing the fuel modifies the average combustion temperatures affecting the thermal tension limits by possibly reducing them. The modification of the gradients and maximum pressure valves in the combustion chamber will influence the mechanical stress although the last one is not normally significant. A deeper knowledge of bio-oil combustion process is necessary to know the exhaust emissions performance.

4.3.- Durability and reliability of the injection system. The durability and reliability of the injection system of a conventional-fuel diesel engine are conditioned by the three following factors: working temperatures, internal parts loading and wear-out of the injection system internal elements (plunger, cylinder, delivery valve, pintle and nozzle). Using bio-oil, the injection system would be one of the most problematic issues; the low pH requires the use of stainless steels or special materials. The lubricant quality of bio-oil together with parameters such as viscosity or oiliness is not well-known at the moment, consequently the reliability and durability of all the injection system elements must be tested if they are stainless.

4.4.- Emissions. Due to the oxygen existing in the bio-oil formulation together with small quantities of nitrogen that some bio-oils contain, it is likely that the NOx ($NO + NO_2$) emissions are somehow higher for the same maximum power than with diesel oil, although a likely reduction of the local combustion temperatures can have the opposite effect. More research needs to be done on this issue. The lower volatility of bio-oil and the difficulties in preheating, if it is used , could lead to an expected increase of the unburnt HC or Organic Gases (hydrocarbons and other oxygenated organic compounds). It is important to take into account the unregulated emissions of particular aldehydes considered carcinogenic that can be present at a greater concentration than with conventional diesel fuels in the exhaust fumes.

Particle emissions (mainly soot) normally known as "smoke", are a function of the local ratio fuel/air in each area of the combustion that depends on the injection system characteristics and their interaction with the air in the chamber. Such emissions are greatly influenced by the non-homogeneity of the air-fuel mixture as well as the average fuel/air ratio. Therefore smoke emission values will depend on the power output demanded by the engine: the greater power the more the smoke.

4.5.- Cleaning. Injection system jamming and sticking up due to bio-oil polymerization which occurs when the engine is stopped, demands the design of an engine with a device capable of removing the bio-oil from the injection system and at the same time capable of cleaning the combustion chamber inner parts. Before stopping the engine and for a period of time, some solvent can be used (ethanol, for example) with some ignition promoter or Cetano improver, to make sure there is no bio-oil left in the system.

On the other hand, the inside cleaning of the engine is a difficult problem to solve with bio-oil; the solution must come from the upgrading or from a sound redesign, of the system: self-cleaning injectors, special valves and nonsticking piston rings.

4.6.- Others. Some other issues to solve when designing or adapting a diesel engine to function with bio-oil are the following: fuel filtering, type and characteristics of the recommended oil, degradation period of the latter, exhaust duct corrosion, etc. Since there is a greater probability of finding traces of suspended solids in bio-oils as well as lignin and sugars, it is reasonable to predict a more intensive filtering system than for that in gas-oils, but similar to the one used with fuel-oils. These consist of a multi-phase filtering with previous centrifugal filters. The acidity of

the fuel and its tendency to form deposits will be the most important factors to take into account when selecting the appropriate lubricating oil.

5 Conclusions

- The main physical and chemical properties of a bio-oil regarding its use in internal combustion engines, qualify it as a "bad" fuel. Nevertheless, modifications can be made in the engine to adapt it to use such a fuel successfully. Likewise, improvement of the fuels physical and chemical properties could be desirable.

- High viscosity and loss of stability with temperature rise, is one of the major problems. Engines with cylinder bore larger than 250 mm (medium speed and low speed engines) could be expected to be the most appropriate.

- For smaller bore engines (high speed engines) reduction of the bio-oil viscosity could be needed. If it would not be possible, injection system modification and/or a high turbulence combustion chamber (prechamber or Esbeltt system) are suitable solutions.

- The main diesel engine modifications to solve the problems caused by bio-oil's "bad fuel" properties are:

  - Bad ignition quality (Cetane Index): cetane improvers, high turbulence prechamber combustion system indirect injection), dual fuel system with a high cetane fuel, preinjection or Elsbett system (two injectors and high turbulence direct injection) are possible solutions.

  - High acidity: suitable materials (stainless steel or other).

  - Poor stability: self-cleaning injectors, a system for cleaning the internal parts of the injection system with ethanol or similar solvent products before stopping the engine, cooled injectors and exhaust valves, etc.

- Fuel upgrading should be desirable. The main objectives for bio-oil use in Diesel engines should be: to reduce viscosity and acidity, to improve stability and to diminish dispersion of physical and chemical properties.

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PRELIMINARY TESTS WITH WOOD-DERIVED PYROLYSIS OIL AS FUEL IN A STATIONARY DIESEL ENGINE

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Abstract

Use of biomass flash-pyrolysis oils as a fuel of the diesel power plant is considered because of the relative insensitivity of diesel engines to the contaminant levels found in pyrolysis oils. As the ignition properties of pyrolysis oil are poor, a pilot injection engine (VALMET DS-420, nominally 84 kW) is applied. Several potential problems related both to production, pretreatment and injection of the oil were identified in preliminary tests. Wear and corrosion were detected in injection needle and pump elements during both bench tests and engine operation. Relatively high carbon monoxide (CO) emissions were analysed in the engine exhaust gas during the test. However, a commercial catalyst installed in the unit removed most of CO and hydrocarbons.

Introduction

A study of the suitability of pyrolysis oil as medium-speed diesel engine (MSD) power plant fuel is underway. A high-speed engine (HSD) was used in this test, because no MSD was available. The availability of the oil was also a limiting factor. Several critical issues in the concept have been identified earlier /1/, and these are being pursued. Some oil analysis are reported in this paper, together with preliminary tests results for a diesel engine fired with pyrolysis oil.

The overall objective of the effort to establish an economic concept for bio-fuel oil utilisation in a MSD power plant will depend on success in several critical areas.

Methods

Pyrolysis Oil Analysis

Mixed-hardwood derived pyrolysis oil employed in the diesel test was provided by Ensyn Technologies Inc. (RTP oil). The oil was pressure filtrated before the test to remove most of the solids. The amount of acetone insolubles in the received oil was 3.6 wt%. The amount of insolubles was reduced to 0.45 wt% in filtration. Some analyses for the RTP oil employed in the engine test are shown in Table 1. For comparison, two typical analyses of diesel power plant fuel oil are shown.

The analytical part of the development effort is critical. The analytical procedures employed and the development work carried out on analytics are described elsewhere /2, 3/.

Table 1. Analysis of flash pyrolysis oil (feedstock hardwood) and fuel oils

		Pyrolysis oil	Light fuel oil	Heavy fuel oil
Heating value[2]	MJ/kg			
HHV		16.5	42.4	40.0
LHV		14.8	40.4	39.0
Density[3]	kg/dm³ @ 15 °C	1.20	0.87	1.01
Viscosity[4]	cSt @ 50 °C	11	6	175
Ash[5]	wt%	0.2	0.01	0.05
Water	wt%	26.6[6]	0.02	0.04
Conradson carbon residue, wt-% [7]		17.8	0.02	12
Flash temperature[8]	°C	53		
Pour point[9]	°C	- 30	0	15
Sulfur	wt%	< 0.01	0.18	2.3
Metals[10]	ppm			
Na		38	0.1	10
K		330		
Ca		100		
Pb		<0.3		
V		0.5	0.01	110
Cl		80		

2) DIN 51900
3) ASTM D 4052
4) ASTM D 445
5) EN 7
6) Karl-Fischer titration, pyridine and ethylenemonomethylglykol-ether (1:4)
7) ASTM D 189
8) ASTM D 93
9) ASTM D 97
10) AAS/ICP

Engine Specification

The engine employed is a four-cylinder VALMET 420 DS. Technical data for the basic engine is given in Table 2. These engines are typically used in tractors. The special test engine is equipped with a pilot injection. A commercial oxidixing catalytic converter is also included.

The engine was equipped with an indicating system for cylinder pressure measurements and with pressure transducers to monitor fuel line pressure. Exhaust gas composition was also measured (NDIR for CO, FID for THC, CLD for NOx and the Bosch method for smoke).

Table 2. Technical data on the VALMET engine /4/

Combustion System		Direct Injection, Turbocharged		
Number of cylinders			4	
Bore	mm		108	
Stroke	mm		120	
Compression ratio			16.5:1	
Speed	r/min	2400		1500
Maximum Power	kW	84		64
BMEP	bar at max. power	9.6		11.7

BMEP = mean efficient pressure

Results

Some oil properties

Three fuel properties are especially important in considering the diesel engine application: viscosity, density, and lower heating value. They are all employed in designing the injection system of the engine.

These basic fuel properties of several RTP oil samples and two additional samples from Union Fenosa (WFPP oils) were determined. These processes are described, e.g., in /5, 6/, respectively. The analyses are shown in Figures 1 - 4.

The range of pyrolysis oil viscosity as a function of temperature is shown in Figure 1. However, it should be borne in mind that the variation of viscosities may be rather wide for different moisture contents of oils. For example, the oil moisture contents of 35 and 18 wt% yield viscosities of 5 and 110 cSt @ 50 °C, respectively. Different oil samples and their viscosities as a function of water content are shown in Figure 2.

Density as a function of oil water content is presented in Figure 3. A similar presentation for the lower heating value of oil is shown in Figure 4.

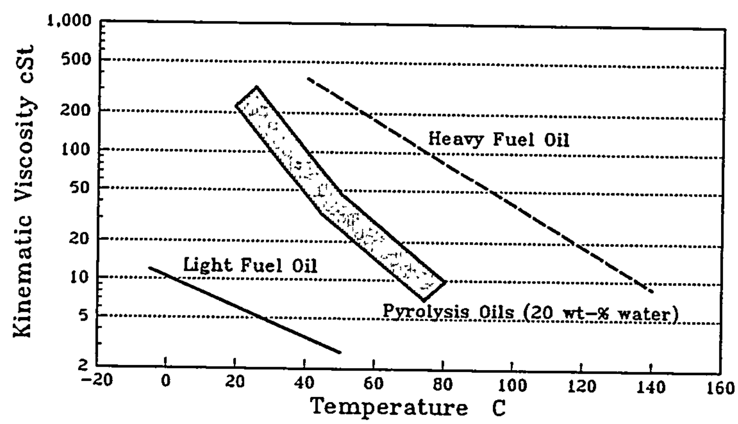

Figure 1. Viscosity of mineral oils and pyrolysis oil

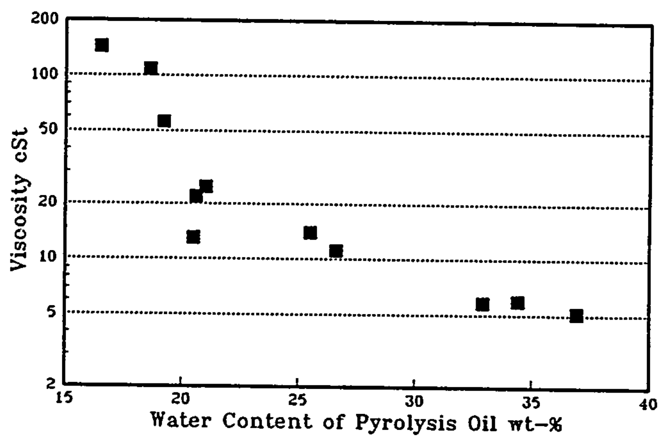

Figure 2. Viscosity as a function of oil water content

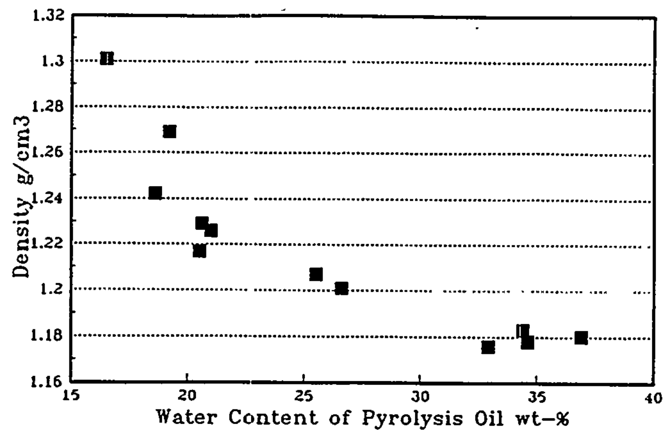

Figure 3. Density as a function of oil water content

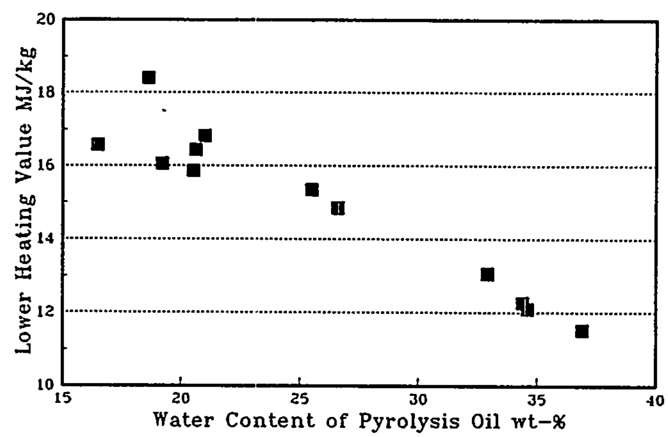

Figure 4. Lower heating value of oil as a function of water content

Diesel Engine Test Procedure

All tests were carried out at about 80 % load (to secure the same power output for all fuels) in steady-state conditions on full load in an engine dynamometer at an engine speed of 1500 rpm, which corresponds to a generator speed of 50 Hz.

When running pyrolysis oil, the engine was started with diesel fuel in the both pilot and the main injection system. As in the preliminary tests with the one-cylinder Petter test engine /1/, the main fuel was then switched to ethanol, and after a while, to pyrolysis oil. Stopping the engine was done in reverse order.

Injection test rig

Prior to the engine test, pyrolysis oil was tested in a bench injection test rig (Figure 5). The test rig includes the same components as the engine injection system. The change of the maximum injection pressure over time is depicted in Figure 6. During the first

hour, the pressure remained fairly constant. However, after two hours a considerable decrease may be seen, and no proper atomisation is achieved. It is believed that a leaking pressure valve causes the decrease.

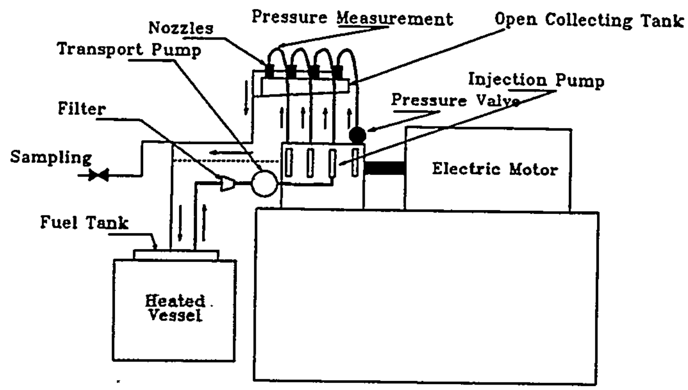

Figure 5. Injection test rig

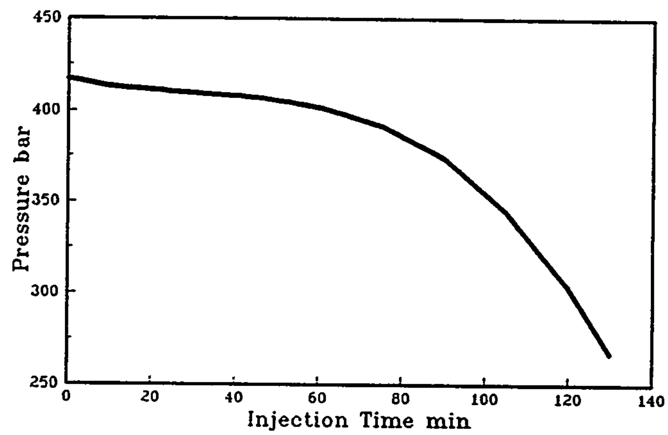

Figure 6. Maximum injection pressure during the test

Preliminary Engine Test Results

Power output on both ethanol and pyrolysis oil was limited by the capacity of the injection pump. In the pilot mode, the engine worked very well on both ethanol and pyrolysis oil.

The BMEP was at the same level in all combinations (Table 3). The pilot-injection system reduced the pressure gradient slightly. Due to the higher amount of fuel injected with both ethanol and pyrolysis oil, the total combustion duration was longer with these fuels compared with that of diesel.

Pyrolysis oil gave the lowest engine efficiency, 38 %, which is quite close to the value with normal diesel operation. Injection duration with pyrolysis oil was long compared with diesel operation. Shortening the injection duration would probably result in an increase in engine efficiency.

Compared to diesel, the NO_x emission was lower and the engine efficiency was slightly higher on ethanol (Table 4). The hydrocarbon (HC) emission increased with ethanol. With pyrolysis oil NO_x emission was about half of that with diesel. The exhaust temperature was some 60 °C lower with pyrolysis oil. The CO emission was very high, roughly 10 g/kWh. However, after employing the oxidizing catalyst, both CO and hydrocarbon emissions were significantly reduced. The smoke number (corresponding to particulates in exhaust gas) was rather low with pyrolysis oil. Using pyrolysis oil in the pilot concept reduced both mechanical (pressure gradient) and thermal stresses (combustion and exhaust temperatures) compared with the original diesel configuration.

Already the short test runs with pyrolysis oil demonstrated, however, that engine component deterioration can be a serious problem with pyrolysis oil. Severe wear was found in the injector needles. This could be a result of a combination of the acidic fuel and abrasive particles in the fuel. This problem requires further attention.

Table 3. Engine performance

Main fuel	BMEP bar	Share of pilot fuel %	Efficiency %
Diesel	9.1	8.3	39
Ethanol	9.1	8.6	40
Pyrolysis oil	9.1	7.9	38

BMEP = brake mean efficient pressure

Table 4. Engine emissions

Main fuel	NO_x	CO before cat.	CO after cat.	THC before cat.	THC after cat.	Smoke number[a]
	g/kWh					
Diesel	7.1	1.8	0.1	1.7	< 0.1	2.7
Ethanol	4.6		0.1		< 0.1	0.5
Pyrolysis oil	3.2	9.9	0.1	1.3	0.4	0.7

a) Bosch-units
CO = Carbon monoxide
THC = Total hydrocarbons
NO_x = Nitrogen oxides

Discussion

Production of oil with a consistent quality has not yet been established, which is one of the most critical issues in the power production concept studied. Consistent oil quality is a necessary requirement for a diesel engine application. It will not be possible to adjust engine injection corresponding to a wide range of fuel properties.

Several potential problems were identified in the preliminary tests. Wear and corrosion were detected in injection needle and pump elements during both bench tests and engine operation. Relatively high CO emissions were analysed in the engine exhaust gas during the test. However, the commercial catalyst installed in the unit removed most of CO and hydrocarbons.

For commercial operation, the injection system has to be re-designed. New materials have to be employed. After new parts have been manufactured, long term engine tests should be carried out.

Acknowledgements

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FUEL-SPECIFICATION CONSIDERATIONS FOR BIOMASS LIQUIDS

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ABSTRACT

A review of the physical and chemical properties of various biomass pyrolysis oils suggests that they will require special consideration for use in current gas turbines without some system modifications. A new balance between fuel quality and engine design characteristics will have to found for the effective use of these liquids. Unfortunately, the values of many critical properties are beyond the range of experience with any distillate fuel, residual fuel, or alternate fuel such as coal liquids or shale oil. Furthermore, there appear to be some characteristics that are new and may require additional considerations in the fuel specification. Some system testing with biomass fuels covering the range of properties will be necessary to develop relevant relationships before design modifications can be made to accommodate biomass fuels and for fuel specifications to be established.

INTRODUCTION

Fuels from biomass, in both liquid and gaseous form, are being considered for use in stationary gas turbines because they come from renewable resources, which are often waste products such as wood chips or rice straw, and because they are considered CO_2 neutral. Pyrolysis liquids from biomass have an advantage over gaseous products because they are more transportable from a processing unit to a power plant; this can ease siting requirements. (Piscitello et al) Also, liquids are easier to store and, therefore, could be used in peaking units.

There has long been a general feeling that gas turbines can burn any fuel, and certainly in comparison to piston engines, both spark ignition and compression ignition, this is true. It would be more correct to say that gas turbines can *be designed* to burn any fuel. However, once optimized for that fuel, or class of fuels, operation of the same gas turbine system on other fuel types may cause reductions in performance and/or durability.

Most gas turbines which are fired by liquid fuels use a clean, petroleum-distillate fuel of low viscosity. A small number of gas turbine systems are fired with crude oil or residual fuels; however, special care is taken to address the problems caused by high viscosity, low hydrogen-carbon ratio, and high levels of contaminants, e.g., sulfur, vanadium, and alkali metals.

In some cases it is possible to derate an engine to make it more tolerant of certain fuel properties or to reduce the impact to acceptable levels. In more extreme cases, one

can expect to have to modify or even redesign certain components in the fuel system or hot section to accommodate variant fuel properties. Generally these modifications can be made with confidence because empirical relationships have been developed between critical fuel properties and relevant design, performance, and durability parameters. (e.g. Lefebvre, Odgers et al)

Such problems are controlled by the engine manufacturer with a fuel specification which describes the limits of critical fuel properties which are known to affect various aspects of fuel storage and handling as well as engine performance and durability. These fuel specifications are developed as a balance of quality, availability, and cost.

FUEL EFFECTS ON GT PERFORMANCE AND DURABILITY

There has only been one demonstration of the use of biomass pyrolysis liquids in a gas turbine engine. (Kasper et al) This demonstration used a small system that had been designed for use with viscous fuels, but is otherwise not typical of conventional gas turbine combustor designs. The results are useful, however, in identifying or verifying certain problem areas. and will be referred to in the following discussions.

A recent study by Moses and Bernstein provides an in-depth summary of the potential impact of using biomass derived fuels, both gases and liquids, on the performance and durability of gas turbine systems for power generation. The following material is a synopsis of the portion of that report dealing with pyrolysis liquids.

Several performance and durability parameters of gas turbine engines are closely related to fuel properties. The major parameters are:

- ignition
- lean stability or turndown ratio
- combustion efficiency
- liner temperatures
- exhaust particulates
- exhaust CO, NOx, and hydrocarbons
- corrosion, erosion, and deposition
- thermal stability
- materials compatibility

When contemplating the use of a gas turbine on a fuel that does not fall within the fuel specification for which the engine was designed, it is necessary to consider the potential effects of the variant fuel properties on these areas of performance and durability, and make design changes accordingly. Generally, the property deviations are small, and the design modifications can be estimated based on known relationships with the various pertinent fuel properties. A demonstration test would then be conducted to verify the performance and durability of the engine on that fuel.

When it becomes apparent that use of the new fuel resource may become more widespread, then a fuel specification is developed for that resource to ensure full compatibility without having to go through the process of redesign, testing, and qualification with each fuel produced. The purpose of the fuel specification is to establish a balance between engine requirements and fuel cost and availability.

The properties of pyrolysis liquids are significantly different than the petroleum distillates for which existing gas turbines were designed; many of these differences are key to engine performance and durability. Table 1 compares relevant properties of some pyrolysis liquids with that of a typical #2 gas turbine fuel. (Czernik et al, Piskorz et al, and Kasper et al) Table 2 summarizes some of the properties of concern and the relevant areas of performance and durability. More recent data reported in this conference shows that new techniques using hot-gas filtration are very effective at reducing the alkali in the biomass liquids from several thousand ppm in the feedstock to almost 1 ppm in the product. (Diebold et al)

The remainder of this paper discusses the significance of critical fuel properties on the performance and durability of gas turbine systems and shows that the magnitude of the variants shown in Table 1, especially viscosity and hydrogen content, precludes the use of current empirical relationships for the basis of necessary design modifications and a corresponding fuel specification.

ATOMIZATION AND BOILING POINT DISTRIBUTION

Many performance and durability characteristics of gas turbines are fundamentally dependent upon the burning time of the largest fuel drops in the fuel spray. The burning time is determined by the quality of the atomization and, usually to a lesser extent, the boiling point distribution of the fuel. When fuel droplets are too large to vaporize and burn out in the time scale of the primary zone, parameters such as stability, emissions, combustion efficiency, and flame radiation are all degraded. Any evaluation of the combustion characteristics of pyrolysis liquids must begin with adequate atomization.

The fuel properties most closely associated with atomization are viscosity, surface tension, and density; the relative importance depends upon the type of atomizer. The pressure swirl atomizer is a typical atomizer and has the following general relationship between the Sauter mean diameter (SMD) and the viscosity, υ, the surface tension, σ, and the density, ρ:

$$\mathrm{SMD} \approx \upsilon^{0.16}\ \sigma^{0.6}\ \rho^{0.2}$$

For petroleum distillate fuels, viscosity is the most important of these properties because surface tension and density change relatively little between fuels or with temperature. Data has not been available for surface tension of pyrolysis liquids. Figure 1 compares values of viscosity for the pyrolysis liquids of Table 1 with typical values for common gas turbine fuels and several other fluids. (Kasper et al) These data show that

TABLE 1. PROPERTIES OF SAMPLE BIOMASS PYROLYSIS OILS

Property	Typical #2 Fuel	Switchgrass Oils			Oakwood Oils				S. Pine	Var.Woods	Teledyne Pyrolysis Oils (Kasper et al)			
	NREL #	146A	146B	146C	143A	143B	143C	154	151	(Piskorz et al)	0% Char	10% Char	20% Char	30% Char
Viscosity														
cSt @ 25C	3.5	18	71	100	58	17	Undef.	---	---	---	250	450	2238	13,250
@ 35C	2.2	10	30	42	22	10	475	63	42	---	113	138	300	675
@ 45C	1.5	7	12	16	10	6	84	---	---	---	38	100	225	425
Specific Gravity	0.8	1.18	1.16	1.12	1.19	1.13	0.94	1.23	1.21	1.2	1.2	1.22	1.3	1.3
Hydrogen	13-14 wt%	6.3	6.2	6.5	7.5	7.1	7.6	5.0	6.5	6.4-7.1	7.3	6.8	6.3	5.9
Carbon	86-87 wt%	42.5	40.4	47.7	42.4	54.7	49.5	55.6	56.3	53-56	55.9	58	60	62
Oxygen	---	50.9	52.2	45.2	50.0	38.1	42.5	39.2	36.9	---	---	---	---	---
Nitrogen	---	0.3	0.4	0.6	0.1	0.2	0.4	0.1	0.3	---	0.15	---	---	---
Sulfur	0.1-1.0	0.03	0.04	0.03	0.03	0.01	0.02	---	---	---	0.07	0.07	0.08	0.08
Alkali ppm														
Na	<0.5	20	40	40	38	36	52	10	10	---	---	---	---	---
K	<0.5	740	1380	580	32	24	35	40	<10	---	---	---	---	---
Ca	<0.5	490	660	590	33	31	23	80	60	---	---	---	---	---
Ash wt%	0.01	0.79	0.95	0.12	<0.05	<0.05	<0.05	0.05	0.05	---	0.32	2.1	3.8	5.5
Water wt%	0.05	24.4	27.7	18.1	22.6	23.6	32.0	16.9	18.5	18-22	29	---	---	---
LHV Btu/lb	18,500	9440	9964	9619	9161	8430	12,366	9155	9231	---	---	---	---	---
HHV Btu/lb		10,000	10,500	10,200	9700	9070	13,000	9700	9900	---	10,500	10,500	10,450	10,400
Boiling Curve,	See Fig. 2													
IBP, °C		90	95	95	97	99	99	---	---	---	See Fig. 2	---	---	---
FPB, °C		161	139	151	187	184	172	---	---	---	---	---	---	---
% Evap.	>99	58	52	59	60	76	90	---	---	---	---	---	---	---
Residue	<1	42	48	41	40	24	10	---	---	---	45	47	49	51
ph	---	3.54	3.73	3.66	2.59	2.60	2.50	2.8	2.9	2.1-2.8	2.95	---	---	---

TABLE 2. SUMMARY OF CRITICAL FUEL PROPERTIES AND THEIR IMPACT ON GAS TURBINE SYSTEMS

FUEL PROPERTIES	IMPORTANT AREA	PERFORMANCE/DURABILITY PROBLEM
Hydrogen content	Soot formation	Combustor liner life Exhaust smoke Venturi overheating
Hydrocarbon composition Acidity	Materials compatibility with metals and elastomers in fuel system components	Fuel leaks and component damage Health and safety issues
Viscosity and boiling range	Atomization and fuel-air mixing	Ignition and lean blow-out limit Combustion efficiency Gaseous emissions
Thermal stability	Hot fuel deposits	Control valves Atomizers
Contaminants	Deposition, erosion, and corrosion	Turbine blades and vanes

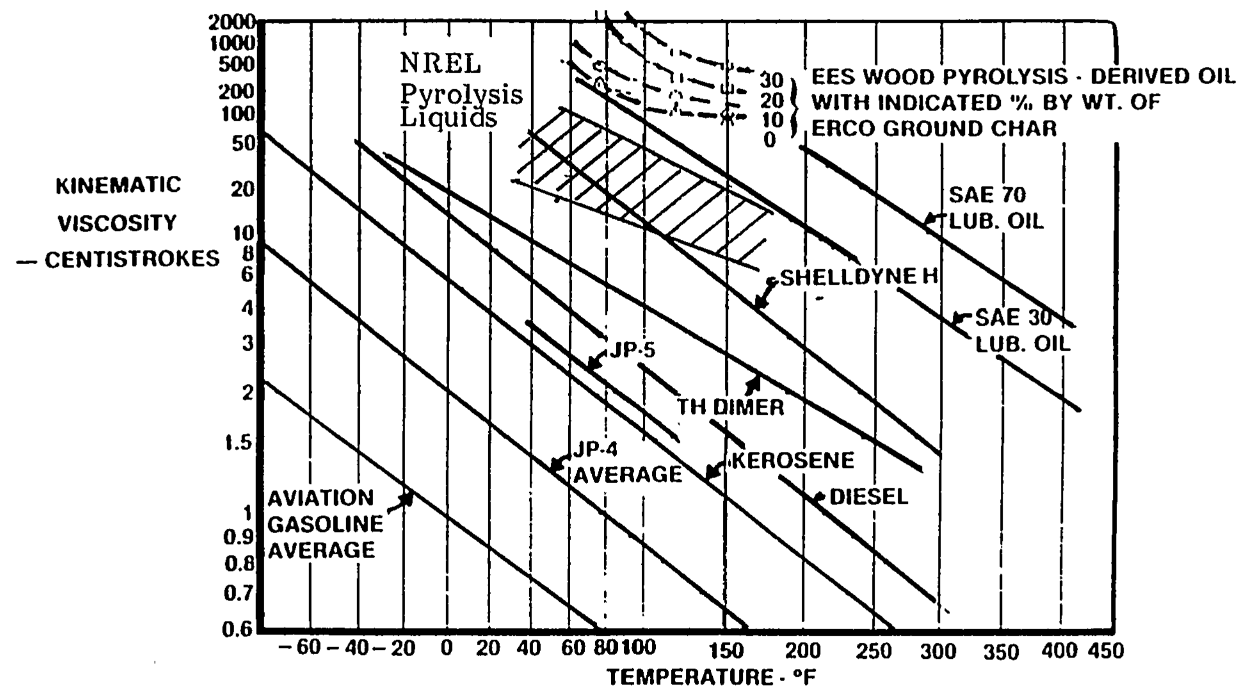


Figure 1. Comparison of Viscosities of Pyrolysis Liquids With Conventional Distillate Fuels and Other Liquids

the viscosity of even the best pyrolysis liquids is about an order of magnitude greater than that of a typical #2 distillate, i.e., "diesel", fuel at 72°F. (It must be noted that only a limited amount of heating can be done to reduce the viscosity of biomass liquids because they have a relatively ow thermal stability; about 200°F seems to be the maximum.)

The specific gravity of many pyrolysis oils is about 1.2 or 50% greater than typical petroleum fuels. These two properties alone would mean that the SMD for pyrolysis oils would be at least 50% greater than that for a #2 distillate. This represents a significant increase in SMD and would result in an increase in burning time of about 100 percent even without changes in boiling point distribution.

The presence of a significant fraction of materials that boil above 650°F, usually a residue in the still, will significantly increase the burning time. The data supplied by NREL on a number of pyrolysis liquids indicated that the amount of distillation residue was between 10 and 50 percent. Figure 2 compares the boiling point distribution of a No. 2 fuel and an aviation fuel with the pyrolysis liquid used by Teledyne in gas turbine combustion demonstration. (Kasper et al) The Teledyne fuel had a residue of 45 percent. Actual burning time can depend on whether the high-boiling fractions, the so-called residue, remain a liquid or pyrolyze into a solid carbon cenosphere during the heat-up and evaporation of the fuel drops.

The residence time of most combustors fall into two categories: about 3 to 5 milliseconds for aeroderivative engines, and 10 milliseconds for large, industrial engines. Designers know how to estimate the burning time of distillate fuels and can thus determine the maximum dropsize permissible and the desired SMD of the fuel spray. The lack of experience in burning pyrolysis oils in gas turbines makes it difficult to estimate the required atomization due to the complications of high viscosity and density along with the distillation residue.

Figure 3 presents the effect of drop size on burning time for various fuels. (Odgers et al) Typical petroleum fuels would lie between curves 4 and 5. Although sufficient data is lacking, a pyrolysis oil might be represented by curve 7 or 8, but could be closer to curve 9. Thus, the droplet lifetime of a heavy fuel oil (#7 or 8) would be at least 10 times that of a conventional gas turbine fuel if the SMD was 50 percent greater to begin with. Judging from the data in Figure 3, the SMD for a pyrolysis oil might have to be in the range of 1/3 to 1/6 of the SMD of a conventional gas turbine fuel, as represented by curve 4 or 5, in order to completely burn out in the same time in a gas turbine combustor.

The presence of water in the fuel may assist the atomization process and greatly reduce the burning time. It has been demonstrated with water-fuel emulsions that the water can preferentially vaporize inside the fuel drop during the drop heat-up period, and the expansion of the steam will shatter the drop into many smaller drops in a phenomenon termed "microexplosion". (Ivanoff et al) While water-fuel emulsions have been shown to improve the combustion efficiency of heavy fuels, it is generally considered that the water must exist as a distinguishable phase dispersed in the fuel, and that concentrations

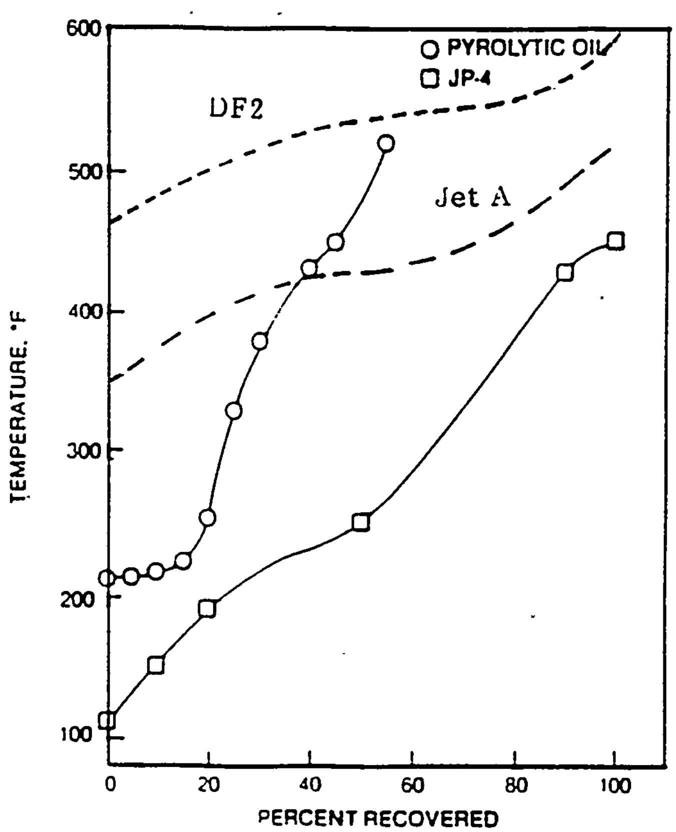
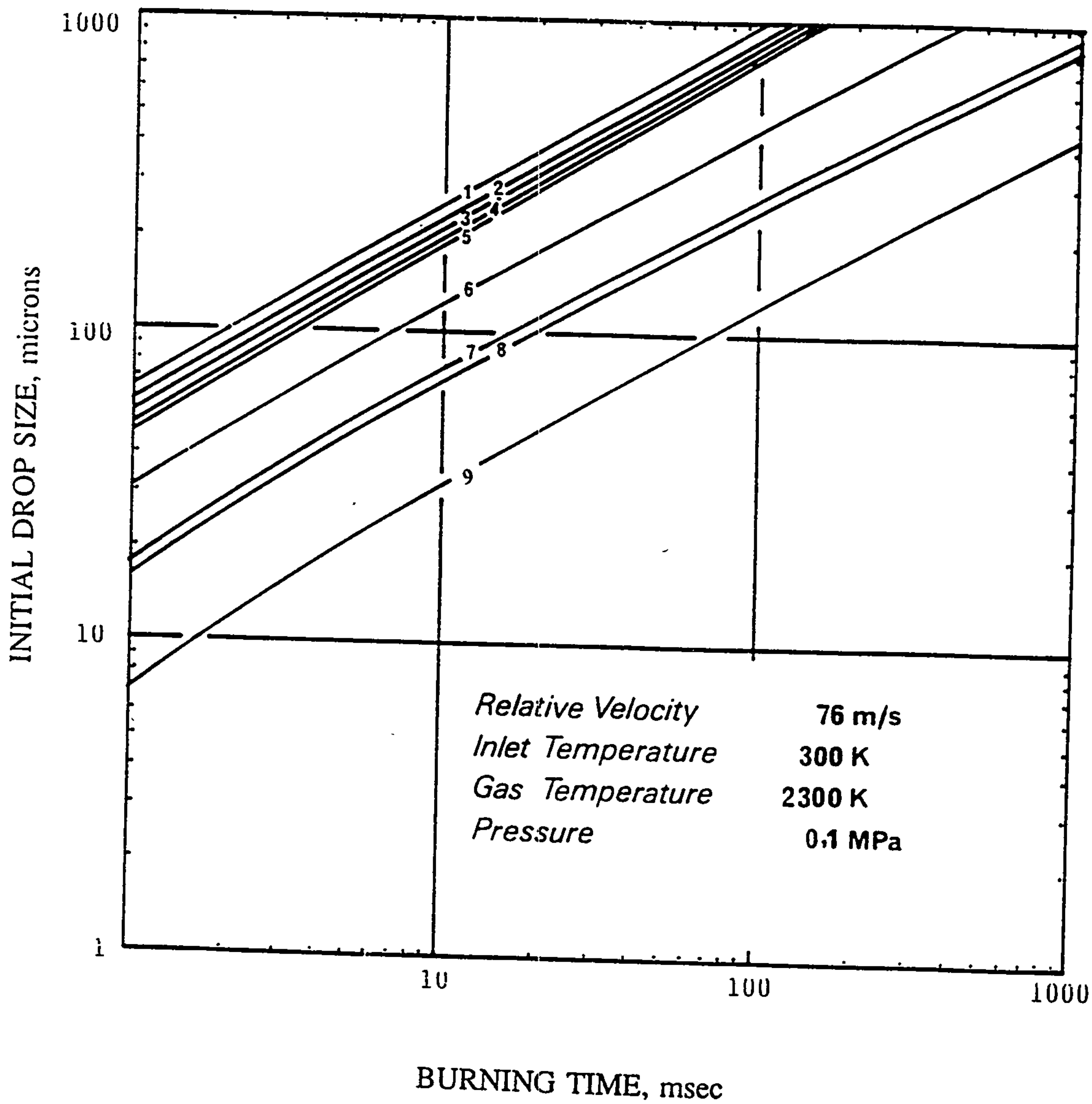


Figure 2. Boiling Point Distribution of a Pyrolysis Liquid Compared with Conventional Distillate Fuels



Legend:

1. Pentane
2. 100 Octane
3. RDE/F/KER210
4. Kerosene
5. Gas Oil
6. Marine Diesel (5% Residue)
7. Pool Fuel Oil (45% Residue)
8. Bunker Fuel (70% Residue)
9. Carbon

Figure 3. Effect of Drop Size on Burning Time for Various Fuels

above 10 percent can reduce combustion efficiency in a gas turbine. (Spadaccini et al) Recently, Wornat et al showed that in single-droplet combustion the presence of the water does significantly reduce the burning time of biomass liquids; the drop size and the time scale of the experiments were large compared to that of gas turbine combustion so, while the application is promising, the results need to be demonstrated in a gas turbine combustor.

Characteristic burning times for fuel sprays need to be determined for biomass liquids containing both high-boiling materials as well as water before atomization requirements can be defined and an atomizer can be selected for a full-scale engine demonstration of pyrolysis liquids. In any combustor demonstration, atomization experiments should be conducted on the atomizer(s) to be used to provide the basis for empirical models of the data for stability, combustion efficiency, emissions, and flame radiation. Unless adequate atomization is assured, no judgement can be made on the compatibility of the fuel and the engine design/modifications. Once "good atomization" is defined, then viscosity limits can be set as part of the fuel specification to ensure this is realized.

EMISSIONS AND COMBUSTION EFFICIENCY

Combustion efficiency is very important in gas turbines not only because poor combustion is a waste of fuel, but also because it is manifested in the exhaust of unburned hydrocarbons and CO. Note that in the case of burning biomass liquids, it would be more appropriate to use "unburned organics" rather than unburned hydrocarbons.

Typically gas turbines operate at design conditions with combustion efficiencies of better than 99 percent. From the fuel standpoint, it is necessary that the fuel be well atomized and evaporated so it can mix with the air and burn in a time scale that is much less than the residence time in the combustor. As previously discussed, burnout becomes increasingly difficult as the fuel becomes more viscous and contains significant amounts of high-boiling materials, both characteristics of biomass pyrolysis liquids. This is illustrated in Figure 4 which compares the combustion efficiencies for four different fuels as a function of combustor residence time. (Lefebvre)

Using a heavier fuel in a gas turbine without modifying the atomizer could reduce the combustion efficiency by 5 to 10 percent. Figure 5 presents data on the combustion of biomass pyrolysis liquids from the Teledyne combustor study which used an atomizer that was tolerant of high fuel viscosity; even so, the combustion efficiency was reduced by 5 percent. (Kasper et al) Consistent with the reduction in combustion efficiency, unburned hydrocarbons were found to increase by over a factor of ten while CO increased by a factor of 6, even at design conditions.

Once the engine design is set, i.e., the atomizer is selected, a viscosity limit must be placed upon the fuel to maintain efficient combustion and low emissions.

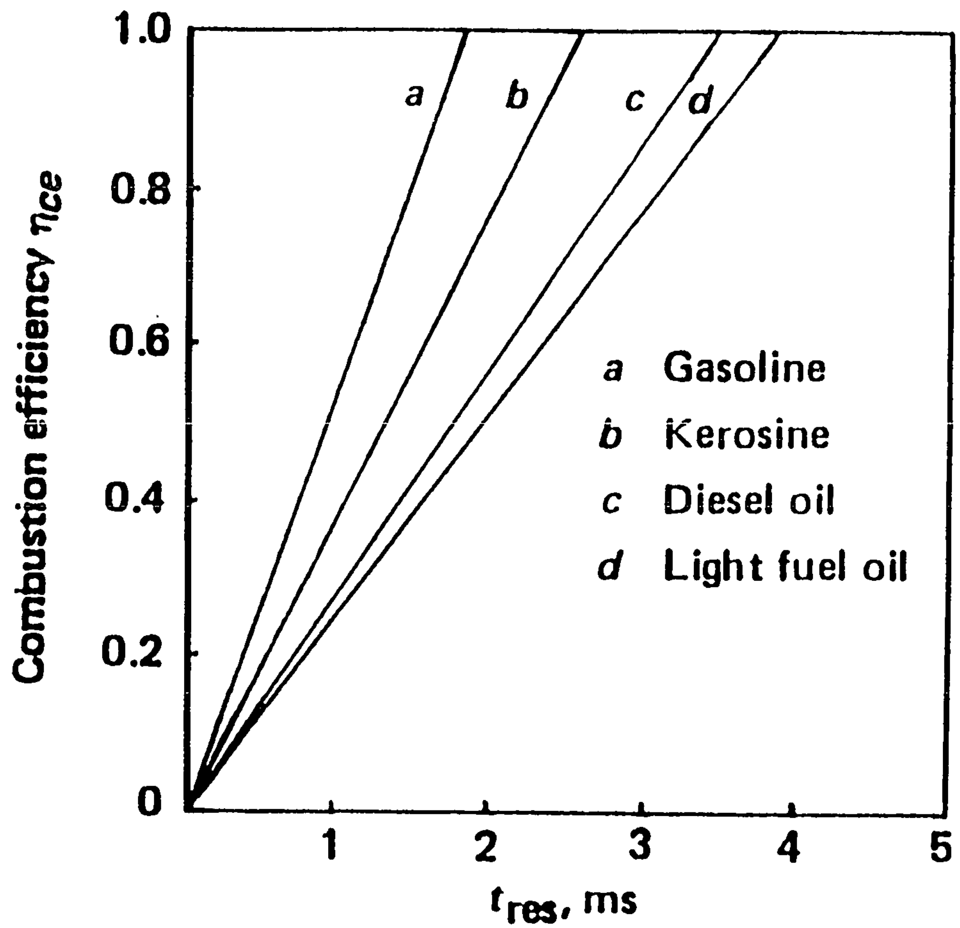


Figure 4. Effect of Combustor Residence Time on Combustion Efficiency

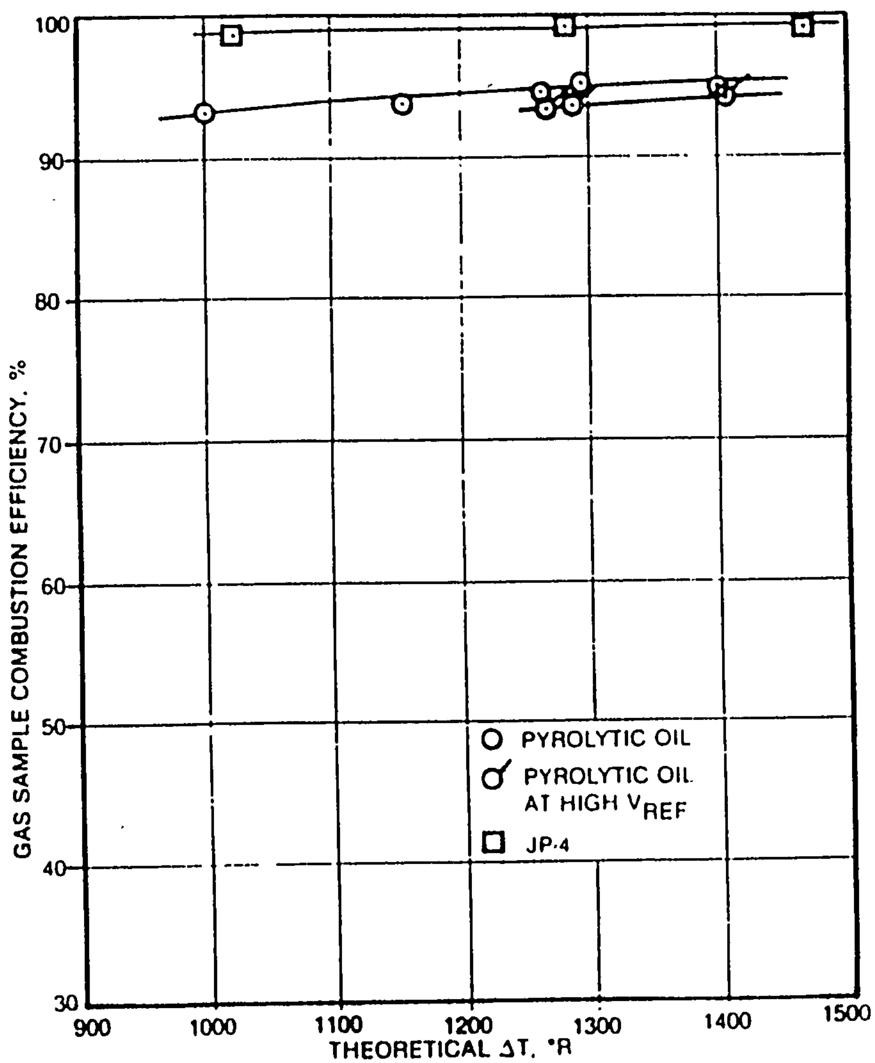


Figure 5. Combustion Efficiency for a Pyrolysis Liquid in a Gas Turbine

The other exhaust emission of concern is NOx, the oxides of nitrogen. There are two primary sources of NOx: thermal NOx, related exponentially to the flame temperature, and fuel-bound NOx, which comes from nitrogen in the fuel. Conventional distillate fuels contain essentially no nitrogen, so thermal NOx is the only mechanism. If the biomass liquid contains no fuel-bound nitrogen, NOx should be the same; however, there could be a reduction in NOx due to the water content of the fuel reducing the flame temperature even if the heating rate is the same.

Some pyrolysis oils have been found to contain as much as 0.9 wt percent nitrogen. The conversion efficiency of fuel-bound nitrogen to NOx is inversely related to firing temperature, just the opposite of thermal NOx. This means that the conversion efficiency of fuel-bound nitrogen to NOx is lowest at the design conditions where a stationary gas turbine for power generation would be operating.

More information is needed on the NOx forming characteristics of pyrolysis liquids to properly set fuel-air ratios in order to meet local NOx regulations. Fuel-bound nitrogen may have to be controlled by the fuel specification.

COMBUSTION STABILITY

Heavy fuels affect the combustion stability of gas turbines as measured by the weak, or lean, extinction limit of the flame. For a given level of atomization, i.e., constant SMD, the flame from a heavy fuel will blow out at a higher fuel-air ratio than a lighter, more volatile fuel. This affects the turndown ratio of the system, of special concern if there is a trip in the circuit. This is also one of the reasons that the gas turbine would have to be switched to distillate fuel before bringing the system down to idle for shutdown.

FLAME RADIATION, LINER TEMPERATURE, AND EXHAUST PARTICULATES

Flame radiation comes primarily from carbon particles formed in the primary zone of the combustor. This radiation is a significant heat load to the liner. Any increases in carbon formation due to fuel changes will result in an increase in combustor-wall temperature and a decrease in the low-cycle thermal fatigue life of the combustor, the leading cause of liner failure. (Moses et al, Foltz et al) Increases in carbon formation also lead to increases in exhaust particulates.

In distillate fuels that are well atomized, it has been shown that the flame radiation and exhaust particulates are well correlated to the hydrogen-carbon ratio of the fuel. (Naegeli et al, two ref.) This is true for fuels containing alcohols and even water when the hydrogen in the water is counted.

When the fuel is not well atomized or when the fuel contains compounds with boiling points above about 650°F, there is an increasing tendency for the last parts of the

fuel drop to pyrolyze and form carbon cenospheres before the drop can be completely vaporized. This is especially true when burning residual fuels or heavy distillate containing some residuum. The presence of these cenospheres can lead to two significant problems:

- an increase in the flame radiation and liner temperature; this will increase thermal fatigue stresses and reduce liner life

- an increase in exhaust particulates which could create an environmental problem as well as increase turbine blade erosion

Figure 6 presents data from a large number of combustor experiments showing that a decrease in fuel hydrogen content results in an increase in liner temperature. (Gleason et al) The data generally falls into two groups: older, rich burning combustors which are more sensitive to hydrogen content, and modern, low-smoke combustors which are relatively insensitive. Liner temperature data from the Teledyne experiment have been added to this data base illustrating both that the hydrogen content of pyrolysis liquids are far lower than previous experience and that the liner temperature increase can be higher than would be predicted by current correlations. General Electric requires a minimum of 12.8 percent in its aeroderivative gas turbines used in power generation.

Pyrolysis liquids are projected to cause an increase in carbon formation for all three reasons stated above:

- very low hydrogen-carbon ratio
- significant concentrations of high-boiling point materials with poor thermal stability
- high viscosity which degrades atomization

A fourth characteristic of pyrolysis liquids, the water content, could partially offset these factors. It has been shown that water-fuel emulsions produce less carbon during combustion and therefore have less flame radiation. There is no way of predicting the net result without some combustor testing.

The extra heat load to the combustor liner that is expected from the use of pyrolysis liquids can be offset by increasing the cooling to the liner. The question remains as to how much cooling will be required since this affects overall efficiency. Establishing a minimum hydrogen-carbon ratio will be a balance between fuel processing costs and efficiency and maintenance costs.

DETAILED ANALYSIS OF EXHAUST HYDROCARBONS/ORGANICS

In addition to the concentration of hydrocarbons discussed above, it is important to analyzes the exhaust organics to determine if any undesirable species are produced because of the fuel chemistry. For example, when alcohols are burned in gas turbines,

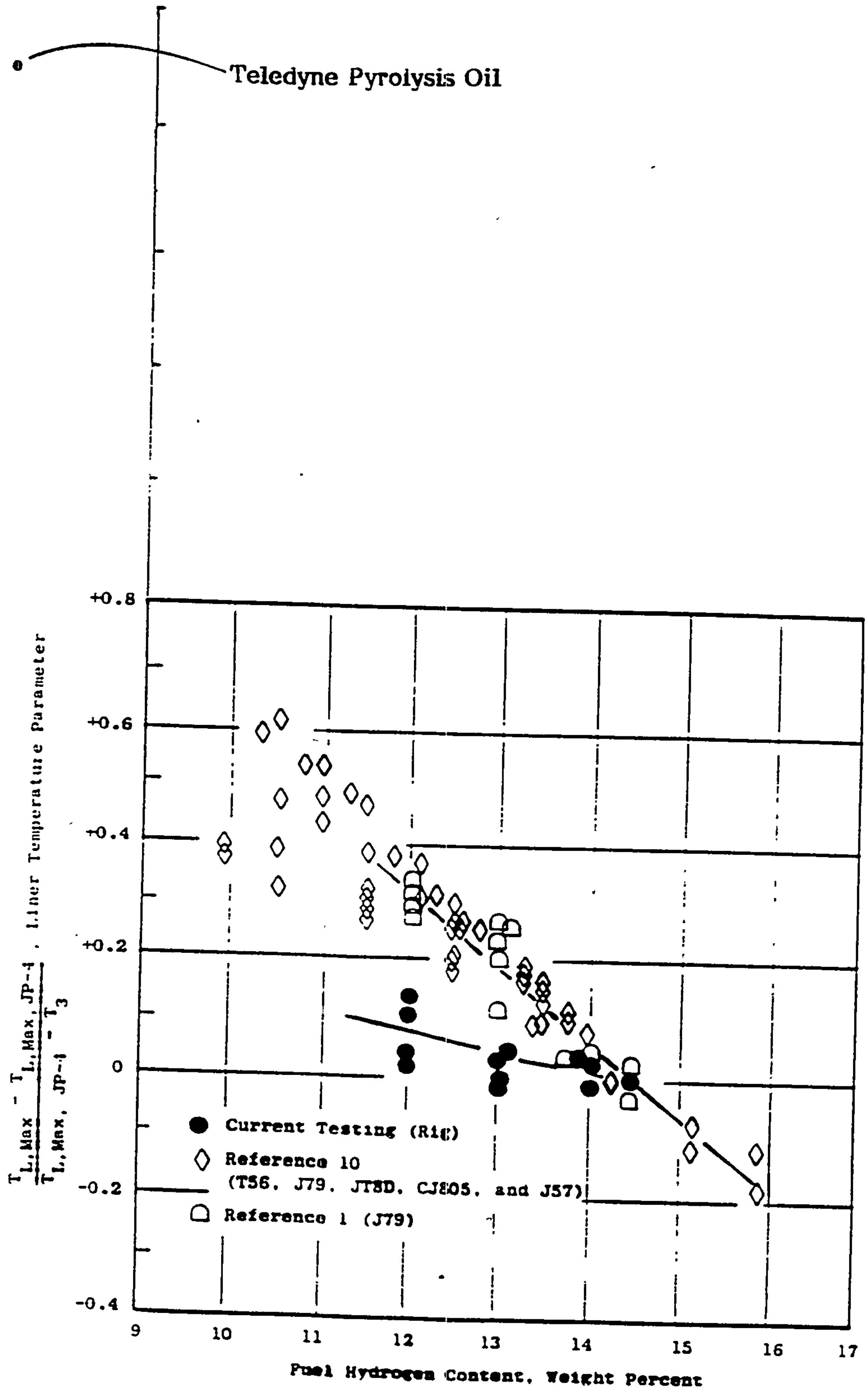


Figure 6. Effect of Fuel Hydrogen Content on Liner Temperature Parameter

there is a significant increase in the acids and aldehydes in the exhaust which have high ozone reactivities and are known irritants. Since pyrolysis liquids contain a significant amount of oxygenated hydrocarbons, it is likely that acids and aldehydes will also show up in their exhaust. Furthermore, incomplete combustion of fuels with high boiling point materials and/or fuel-bound nitrogen generally leads to the presence of polynuclear aromatics (PNA) and other undesirable organics in the exhaust; these are often found on the particulates as a soluble organic fraction (SOF).

The analysis to characterize the exhaust organics should be conducted on three samples: volatiles, semi-volatiles, and the soluble organic fraction on the particulates. The volatiles will primarily be light hydrocarbons of 1 to 5 carbon numbers, but will also contain formaldehyde and acetaldehyde, and their related acids. The semi-volatiles will be the condensible part of the exhaust hydrocarbons consisting of both unreacted fuel components and partially reacted or intermediate species. The semi-volatile fraction and the soluble organic fraction on the particulates should be analyzed for carcinogenic or mutagenic materials such as PNA's, nitro-PNA's, and dioxins.

If such materials are present and can be correlated to certain compounds in the fuel, then either combustor conditions will have to be found where these materials are not produced, or one element of the fuel specification for pyrolysis liquids will have to limit the presence of those compounds in the fuel.

CORROSION

The subject of corrosion is conveniently discussed in three areas:

- alkali sulfate corrosion
- alkali chloride corrosion
- tolerance of thermal barrier coatings

Alkali-Sulfate Corrosion:

This is probably the most serious problem to overcome in the use of pyrolysis liquids in gas turbines. Current fuel specifications are very stringent on the allowable amounts of alkali levels. Usually total alkali refers to "sodium plus potassium" because calcium is usually not significant in petroleum fuels. Allowable levels are in the range of 0.5 to 1.0 ppm of the fuel, and are designed to preclude hot corrosion of the blades. Table 1 shows that some biomass pyrolysis liquids have been found to contain alkali contents that are two to three orders of magnitude higher than currently allowed. Furthermore, the alkali in biomass liquids is difficult to remove by the traditional means of water washing because of the high solubility of biomass fuels in water. Fortunately, recent data reported in this conference shows that new techniques using hot-gas filtration are very effective at reducing the alkali in the biomass liquids from several thousand ppm in the feedstock to almost 1 ppm in the product. (Diebold et al) There was considerable

variation in the data reported by Diebold et al, and it was not clear whether this was due to the accuracy of current analytic techniques for measuring alkali or inhomogenieties in the samples submitted for analysis. Nevertheless, these results are very promising in this critial area.

Because calcium is rarely found in petroleum-derived turbine fuels, the blade materials and coatings are optimized for sodium and potassium. Migration of calcium has been found, however, in coatings that are resistant to sodium and potassium. This problem needs to be verified if the high concentrations of calcium found in the biomass liquids, especially those from grasses cannot be removed.

The real culprits in this corrosion problem are the alkali sulfates produced during the combustion process. The stringent alkali levels in the fuel specification are based upon petroleum derived fuels in which there can be relatively high levels of sulfur, as much as 1 wt%. Available test results indicate that the high-temperature coatings used on turbine blades may be more tolerant of higher alkali levels in the fuel if the sulfur level is very low. If this can be confirmed, a relaxation of the alkali limit would be an important consideration for the fuel specification and would reduce the cost of pyrolysis liquids. Even a slight relaxation would put the allowable levels in the range reportedly achieved by hot-gas filtration. (Diebold et al)

Alkali-Chloride Corrosion:

Conventional gas turbine fuels do not contain chlorine, whereas it is found in some biomass liquids, especially those from grasses. As a result there is no information on the resistance of conventional high-temperature blade and coatings to alkali chlorides. This is a problem that must be further defined. If it is significant, then it must be determined if the solution should come from the fuel specification or the development of resistant coatings.

Tolerance of Thermal Barrier Coatings:

Thermal barrier coatings (TBC) provide protection to the base metal of turbine blades by acting as a thermal insulator. They have also been shown to be beneficial in hot corrosion by separating the base metal from the from the corrosive environment. (Note: Thermal barrier coatings are a different type of coating than the high temperature coatings addressed above. Thermal barrier coatings are ceramic whereas the other are metallic, e.g. nickel aluminides.) TBC have not been tested for their effectiveness or durability in the chemical environments anticipated with biomass-derived fuels, i.e., with high alkali, chlorine, and low sulfur. TBC's may be able to provide sufficient protection to allow the higher alkali levels in these fuels.

THERMAL STABILITY

There is a desire to heat the biomass fuels to reduce their viscosity to improve atomization and combustion performance. Some of the chemical constituents of biomass fuels are apparently unstable at elevated temperatures and decompose forming deposits in the fuel system. There are two approaches that can be taken to address this problem:

- Set a minimum thermal stability limit on the fuel, as is done for aviation turbine fuels, or
- Provide a measure of the thermal stability limit so the user will know how far the fuel can be safely heated.

The latter is considered more practical for land-based turbines since there is greater flexibility in controlling fuel temperatures than in aircraft where the fuel is used to cool the engine oil and other airframe components.

MATERIALS COMPATIBILITY

Materials compatibility falls into two categories: metals, used for storage facilities and fuel system components, and elastomers which are used for seals and gaskets.

Pyrolysis liquids tend to be quite acidic, with pH factors around 3 not too uncommon. This means the fuels would be quite corrosive to mild steel, a common material for storage tanks, fuel lines, valve housings, etc. This was verified in the Teledyne study which also reported no corrosion of stainless steel after seven days at 180°F. (Kasper et al)

The Teledyne study was inconclusive concerning elastomer compatibility with the pyrolysis liquid used. Huffman et al found that the common elastomeric compounds Buna N, Viton, and Neoprene are not suitable for use with pyrolysis liquids, but that EPDM, teflon, and polypropylene are satisfactory.

A consistant fuel is important for materials compatibility. Even though the elastomers selected might be compatible with the original fuel, another pyrolysis liquid with a significant change in fuel composition might be incompatible, resulting in leaks or component damage.

SUMMARY

A review of the physical and chemical properties of various biomass pyrolysis oils suggests that they will require special consideration for use in current gas turbine systems. Compared to distillate fuels, they are very viscous and acidic, have a low hydrogen-carbon ratio, high density, high tar and alkali content, although recent results with hot-gas

filtration show results that are close to current specification levels. Conventional methods employed with residual fuels, such as heating to reduce viscosity and water washing to remove alkali, will not be effective with biomass fuels because of their low thermal stability and high water solubility. Alternately, the presence of the high water concentrations may aid in atomization and the reduction in soot and particulates.

A new balance of fuel quality and engine design characteristics will have to found for the effective use of biomass liquids. Unfortunately, the values of many critical properties are quite beyond the range of experience with any distillate fuel, residual fuel, or alternate fuel such as coal liquids or shale oil. Furthermore, there appear to be some characteristics that are new and may require additions to the fuel specification. Some system testing with biomass fuels covering the range of properties will have to be done to develop relevant relationships before design modifications can be made to accommodate biomass fuels and for fuel specifications to be established.

Of greatest concern are the following:

- Effects of physical properties and water content of biomass pyrolysis liquids on atomization, combustion efficiency, and gaseous emissions

- Effects of physical and chemical properties, including water content, of pyrolysis liquids on soot formation and hence on flame radiation, liner temperature, and particulate emissions

- Effects of chemical composition of biomass liquids on the composition of the exhaust organics/hydrocarbons

- Effects of high alkali content in the presence of chlorine and/or low sulfur in biomass fuels on corrosion of turbine blades

- Fuel thermal stability and the ability to heat the fuel to reduce the viscosity and improve atomization

- Compatibility with metals and non-metallic elastomers and seal used in fuel systems because of the acidic nature and the unusual organic compounds in pyrolysis liquids

Developing a fuel specification for pyrolysis liquids is necessary to assure fuel quality and price so that engine development costs can be minimized and satisfactory performance and durability guaranteed.

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FIRING FAST PYROLYSIS OIL IN TURBINES

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ABSTRACT

This paper describes an international cost shared development program aimed at firing of fast pyrolysis bio-fuel oil in a gas turbine engine for power generation. Bio-fuel oil offers potential for direct use in gas turbines and commercial marketing of power generation systems worldwide. Hawker Siddeley Canada Inc., has over forty years experience in the industrial gas turbine industry and the capability to develop and market bio-fuel oil power generation systems.

The main objectives of the program are: to operate a small gas turbine on bio-fuel oil and to optimize the fuel production based on performance, emissions and practical commercialization. Although some technical limitations exist there are available techniques to address these limitations which are to be examined.

The turbine engine selected as the test vehicle is a 2.5 MW class - GT2500 engine designed and built by Mashproekt in the Ukraine. The standard operating conditions and layout of this engine provide flexibility in optimization of the combustion system to accept lower than conventional grade fuels.

INTRODUCTION

The rapid rate at which our usage of fossil fuels is releasing carbon dioxide emissions into the atmosphere has raised international concern and has spurred intensive efforts to develop alternative, renewable sources of energy that would have a minimal detrimental impact on our environment.

Biomass (i.e., wood waste) derived fuels substituted for fossil fuels could help reduce carbon dioxide emissions that are thought to be contributing to the greenhouse warming of the earth, since biomass absorbs the same amount of carbon dioxide in growing as it releases when consumed as fuel. In contrast to most fossil fuels, bio-fuel oils contain negligible or zero levels of sulphur. Hence, they do not contribute to acid-rain problems, or require expensive stack gas clean up.

Biomass energy could potentially satisfy a substantial proportion of the world's energy needs if technologies were developed for:

a) efficient fuel production, i.e., to convert various forms of biomass feedstock to a liquid or gaseous fuel, at competitive costs;

b) efficient fuel combustion, to be able to utilize these fuels in a power generation system for generating electricity at high efficiency, low capital cost and minimal detriment to the environment.

Bio-Fuel Oil

The fuel being considered in this program is produced by Ensyn Technologies through their Rapid Thermal Process (RTP) using a wood waste feedstock to ensure the highest fuel quality. Ensyn has proven through combustion testing and commercial experience that their fuels can burn readily in a self sustaining mode. In addition, the potential for competitive overall costs exist with a practical fuel process and combustion design.

Potential Markets

Markets exist worldwide for the application of renewable and environmental fuels, and energy systems. In Europe the high cost of electricity combined with environmental concerns, which include incentives, provide an ideal market. The new costs for waste disposal and growing environmental concerns in North America combined with the need to identify renewable energy sources should provide a significant future market. This new market will also offer potential retrofits of North American industrial engines for bio-fuel oil power generation. In addition, Asia and the Pacific rim have abundant agricultural waste and limited power facilities offering another significant market.

Hawker Siddeley Canada Inc.

Hawker Siddeley Canada Inc., Orenda Division has over forty years of experience in industrial gas turbines, including design, packaging marketing and repair and overhaul. Orenda is presently packaging and marketing a complete line of power generation facilities using Mashproekt, a Ukrainian gas turbine engine manufacturer, industrial gas turbine engines. The facilities range in power output from 2.5 to 25 MW, as shown in Figure 1. These engines will be the heart of Orenda packaged generation facilities which will be custom designed for each user based on their specific application, see Figure 2. In addition, Orenda will back these facilities by providing all required sales, service and future repair and overhaul requirements.

OBJECTIVES

The objectives of our program are divided into two phases, where Phase I is a proof of principle and Phase II is the development and durability testing of a commercial product.

Phase I will be used to demonstrate the feasibility of utilizing the bio-fuel oil derived by Ensyn as a fuel for a combustion turbine engine. The tasks for engine development have been identified as: characterization of bio-fuel oil, fuel systems development, engine performance evaluation, component durability assessment and monitoring of emissions. While concurrently the fuel production process will be examined to optimize the fuel based on practical commercialization, with respect to: performance, emissions, component durability and cost.

Phase II will include commercialization of the Phase I test vehicle through development of fuel systems, engine combustion and turbine section durability. Accelerated engine tests will be used to assess long term component durability, system performance and maintenance periods. The final goal is to locate and install a pilot plant for power production.

TECHNICAL LIMITATIONS

Although potential exists, some technical limitations also exist including: high fuel viscosity, fuel acidity, high ash content, lower heating value and alkali content. Techniques exist in both the tailoring of fuel process parameters and the modification of gas turbine engine systems to deal with these limitations. The bio-fuel oil is not a petroleum fuel and cannot be practically modified through process conditions to provide petroleum fuel properties. In addition, gas turbine engines cannot be practically modified to burn bio-fuel oils which have not been optimized.

To overcome high viscosity, the bio-fuel oil can be preheated just prior to combustion, however, it cannot be held at temperature for extended periods and the preheat temperature should not exceed 90°C. This limit is a result of bio-fuel oil decomposition which can occur at or above this temperature if held for more than a short period. The bio-fuel oil acidity can be accounted for by the selection of applicable materials for the fuel systems and coating selection for the turbine section components. Ash levels have been significantly reduced using filtering techniques during processing. The lower heating value of the bio-fuel oil will require ignition on conventional fuels and an increased fuel flow resulting in nozzle and combustor modification for commercial application. The alkali content needs to be addressed through improvements in fuel processing, reduction by fuel additives and minimization of component degradation by the use of advanced protective coatings.

TEST VEHICLE

Initially, the main concern of the program was to review and select a small gas turbine, which was best suited to achieve the objectives. The Mashproekt GT2500 engine has been identified as an ideal candidate for the bio-fuel oil program test vehicle.

Based on Orenda's industrial power generation business, mentioned previously, the GT2500 engine will have strong company support since it is representative of an entire line of engines

which Orenda is packaging, marketing and providing both future service as well as repair and overhaul. In addition, since this engine was designed and will be sold for power generation, the program is closer to commercialization than for a similar aero-derivative. If the demonstration was carried out using a small aero-derivative the engine specific developments would not be applicable to other engines and therefore, the final installation would not benefit from the previous modifications.

Technically the GT2500 offers distinct advantages over other engines. Unlike the aircraft derivatives which use jet fuel (JP4), this small industrial engine uses Russian diesel, which has physical properties closer to bio-fuel oil, as a standard operational fuel. The diesel fuel nozzles use a dual passage system which allows more flexibility for liquid fuel operation. A positive flame ignition system offers potential for bio-fuel oil starting. Advanced coating systems are used as standard for hot section durability and may provide sufficient protection against contaminants. The critcal factor is that the engine offers the ability to easily modify the entire combustion system, since the design incorporates "Silo" type combustion chambers which are located above the engine, as shown in Figure 3.

In addition to the suitability of the engine for bio-fuel oil operation, the relationship with the original engine manufacturer is necessary to provide design information and operational characteristics needed for testing and design of engine modifications.

TEST PROGRAM

Task 1: Fuel Property Characterization

The fuel has been characterized based on two production techniques for: calorific value, flash point, temperature dependence of viscosity and density, surface tension, moisture, ultimate analysis (C,H,S,N & O), ash content, particulate content, pH and corrosion of standard materials. The results are provided in detail in Table 1 for the two production techniques developed by Ensyn Technologies. Bio-fuel oil A is a research level sample while bio-fuel oil B has been produced commercially and can be produced in large quantities. Alkali content of the two fuel samples is presently being compared as well as the balance of the Alkali in the filtered particulates versus the complete sample.

The low heating value of bio-fuel oil will require an increased fuel flow or derating of the engine with respect to diesel operation. The viscosity can be improved to within specified diesel values using a preheat between 60-90°C, however the viscosity of bio-fuel oil B appears to be a problem even with preheat. The moisture content is not contamination but part of the fuel make up and therefore cannot be compared directly. In addition, a lower moisture content results in a significant increase in viscosity. The ash and particulate content has been significantly reduced by modifications to the processing. The particulate content of bio-fuel oil A has been reduced to within diesel specification, while for bio-fuel B the particulate content is higher but still better than in the past. The pH was found to be below specified levels, however the results of

corrosion tests, given in Figure 4, have shown that even at 70°C the bio-fuel oil does not corrode stainless steel, which is the standard fuel system material on most gas turbine engines.

Task 2: Test Plan Development

The test plan development has two main objectives, the first to select a test vehicle and the second to prepare a detailed test plan which covers all aspects of the engine testing. The test vehicle has been selected as discussed earlier and the preparation of the detailed test plan is in progress. The test plan will include, but not be limited to: test procedure development, desired results, test vehicle support, accessories, instrumentation, data acquisition and analysis of test data.

Task 3: Fuel Handling and Engine Fuel System

A complete design of the fuel system is required based on the need for fuel preheating and dual fuel operation. To assist in the fuel system design, atomization testing of fuel nozzles and a coking evaluation will be carried out prior to detailed design efforts. The system design will include: the fuel delivery system development, flow measurement and control as well as fuel storage systems.

Task 4: Engine Instrumentation

To ensure that all the data required for evaluation of engine performance and durability, operating on the bio-fuel oil, comprehensive engine instrumentation will be installed on the test cell engine. The data collected will include, but not be limited to: engine speed, air and fuel flow rates, compressor discharge pressure and temperature, combustor discharge pressure and temperature, combustor liner temperature, turbine inlet temperature and stationary component temperatures. This instrumentation, combined with a high performance data acquisition system, will provide the required data for calculation of combustion, cycle and overall engine efficiencies as well as providing baseline data for the evaluation and design of long term component durability.

Task 5: Endurance Testing and Engine Performance

Component and specimen level hot corrosion endurance tests will be used to evaluate component durability under bio-fuel oil operation. High temperature, long term combined furnace and bio-fuel oil exposure tests will be used to identify the damage effects and mechanisms. Flame tunnel testing will be used to simulate the engine environment by exposing gas path components to a bio-fuel oil combustion flame at locations which match engine operating conditions. The flame tunnel will also provide basic combustion information and preliminary emissions data. A full scale fuel system test will be carried out, prior to engine testing, to ensure that the system operates within specifications.

Engine performance tests will be carried at the test cell level using bio-fuel oils produced by varying process conditions. The engine tests will provide the information essential to redesign the engine for commercial application. The instrumentation, discussed previously, will provide information on combustion, performance, emissions and component durability. In addition, the varying process conditions will provide data for optimization of the fuel production process.

Task 6: Phase II Planning

The data collected from all of the Phase I tasks will be used to prepare a detailed plan which covers the modification of the test engine for commercial application as well as identifying accelerated test cycles and a long term durability test program.

CONCLUSIONS

1. Potential exists for the direct use of biomass derived fuels in Orenda's line of gas turbine engine power generation packages. Although some technical limitations exist there are available techniques to address these limitations which are being examined.

2. The characterization of two Ensyn fuel samples, prepared under different process conditions, has been completed and the critical fuel properties have been identified, with the exception of the Alkali content which is in progress.

3. The Mashproekt GT2500 engine has been identified as an ideal candidate for the bio-fuel oil program test vehicle and an agreement has been reached for the acquisition of the test engine.

4. A detailed test plan is being prepared and preliminary fuel testing and system design are in progress. The outstanding tasks required to successfully complete this program have been identified and are in the planning stage.

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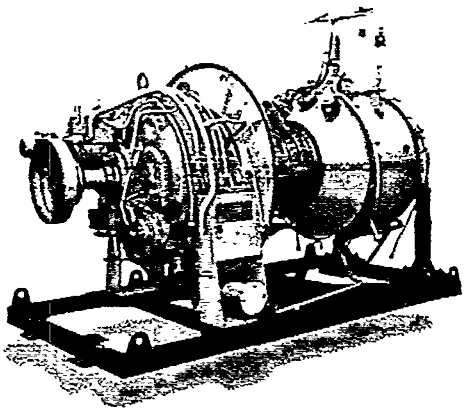
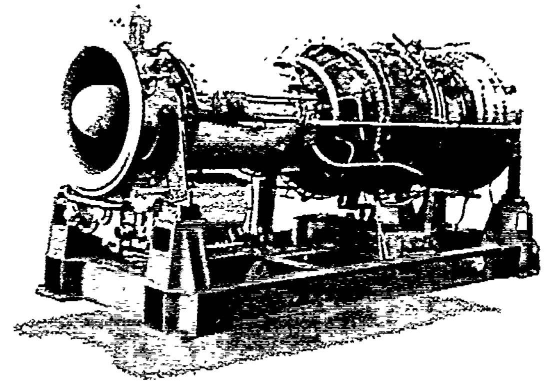
National Research Council Canada
United States Department of Energy, NREL
Government of Ontario, Ministry of Environment and Energy, EnerSearch
Ente di Sviluppo Agricolo in Umbria, E.S.A.U.

Table 1: Bio-fuel oil Properties and Comparison to Diesel Specification

Analyses	Standard	Units	Bio-fuel oil A	Bio-fuel oil B	Diesel Spec.
Calorific Value	LECO AC-300	MJ/kg BTU/lb	16.8 7243	20.0 8647	42.0 18107
Flash Point	ASTM D93-90	°C	60	63	35-60
Kinematic Viscosity	ASTM D445-88	cSt			
at 20°C			~50	2004	1.5-6.0
at 40°C			14.33	-	
at 50°C			9.116	137.4	
at 60°C			6.237	56.28	
at 70°C			4.497	34.39	
Moisture	ASTM D-1744 (Karl Fisher Titration)	wt%	21.0 23.5	19.1 -	0
Ultimate					
Carbon	LECO CHN-600	wt%	41.1	49.0	-
Hydrogen	LECO CHN-600	wt%	7.58	7.21	-
Sulphur	ASTM D-1552	wt%	< 0.01	-	0.5
	ASTM D-3120	ppm	91 (0.01%)	0.013	-
Nitrogen	LECO CHN-600	wt%	< 0.05	-	-
	ASTM D-4629	ppm	520 (0.05%)	0.04	-
Ash	ASTM D-482	wt%	0.04	0.04	0.01
	ASTM D-482	wt%	0.01	-	-
Oxygen	PE-240	wt%	50.6	43.0	-
Density	ASTM D4052-91	g/ml			
at 20°C			1.208	1.238	0.83-0.86
at 30°C			1.199	1.229	
at 40°C			1.190	1.211	
at 50°C			1.186	1.207	
at 60°C			1.171	1.197	
Acetone Insolubles	-	%	0.098	-	0.01
Surface Tension	Fisher Surface Tensiomat at 25°C	µN/m	34.2	38.8	-
pH	Sargent - Welch pH meter	pH	2.46	2.39	5
Particulate Content	PTFE Type Millipore Membrane Filtration				
5 µm		wt%	0.019	0.592	-
1 µm		wt%	0.001	0.009	-



GT2500



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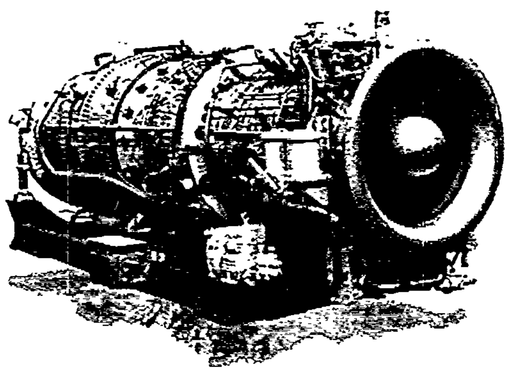
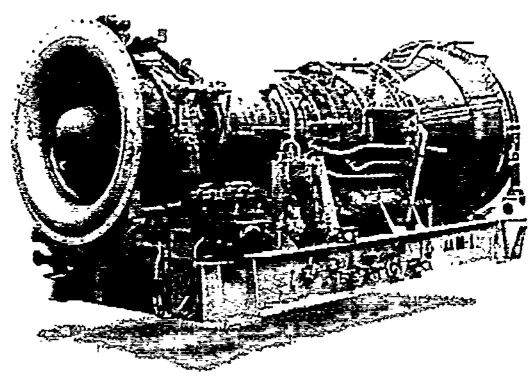


GT15000



GT25000

Figure 1: Orenda/Mashproekt Line of Industrial Gas Turbine Engines.

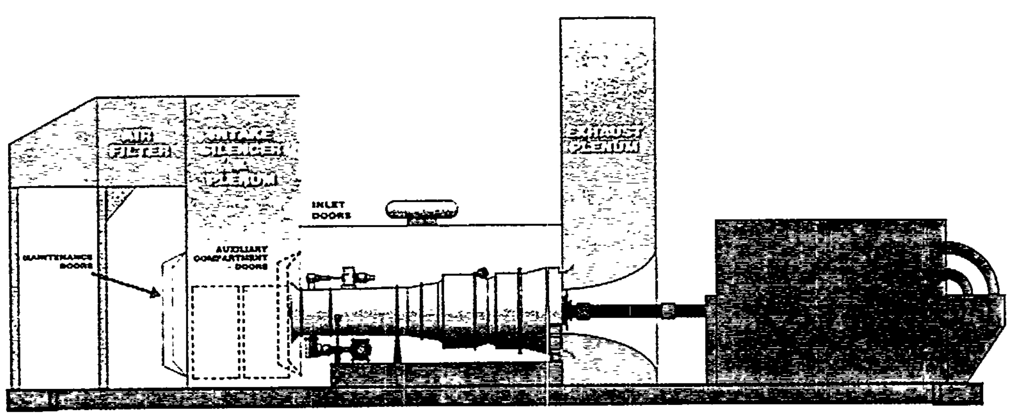


Figure 2: Customized Orenda Industrial GT15000 Power Generation Package.

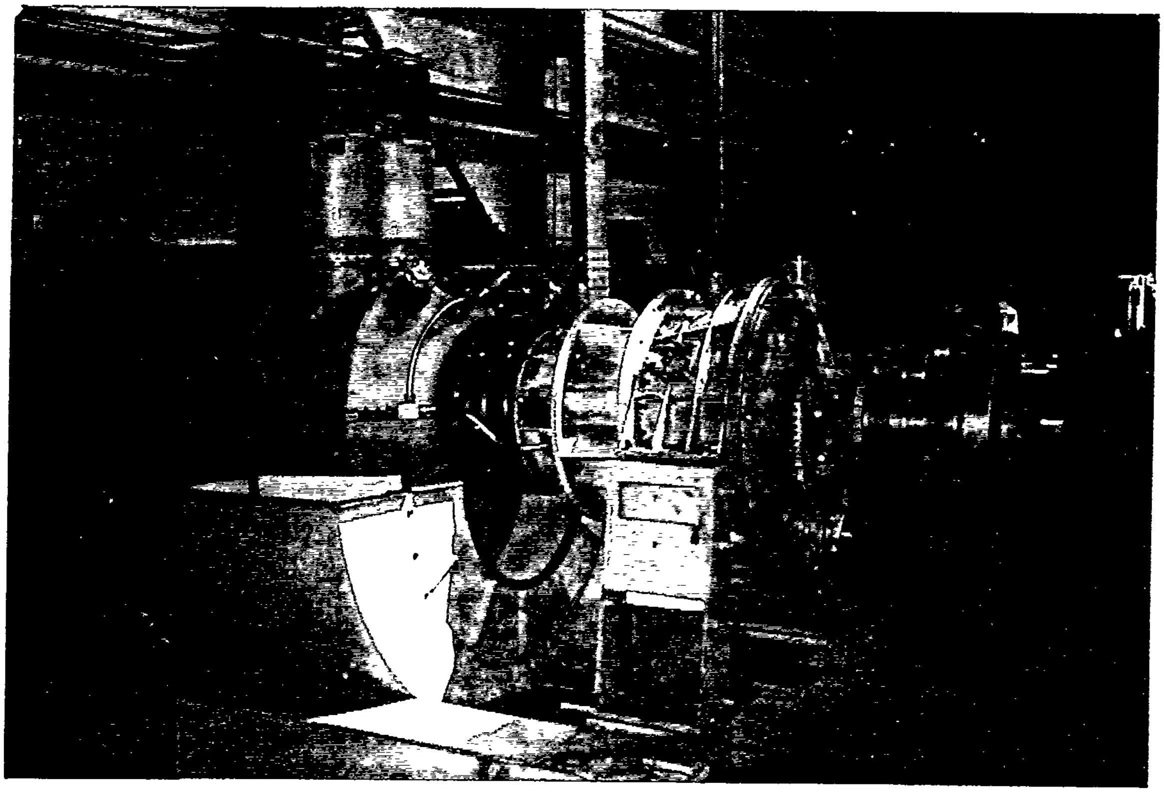


Figure 3: Orenda/Mashproekt GT2500 Gas Turbine Engine.

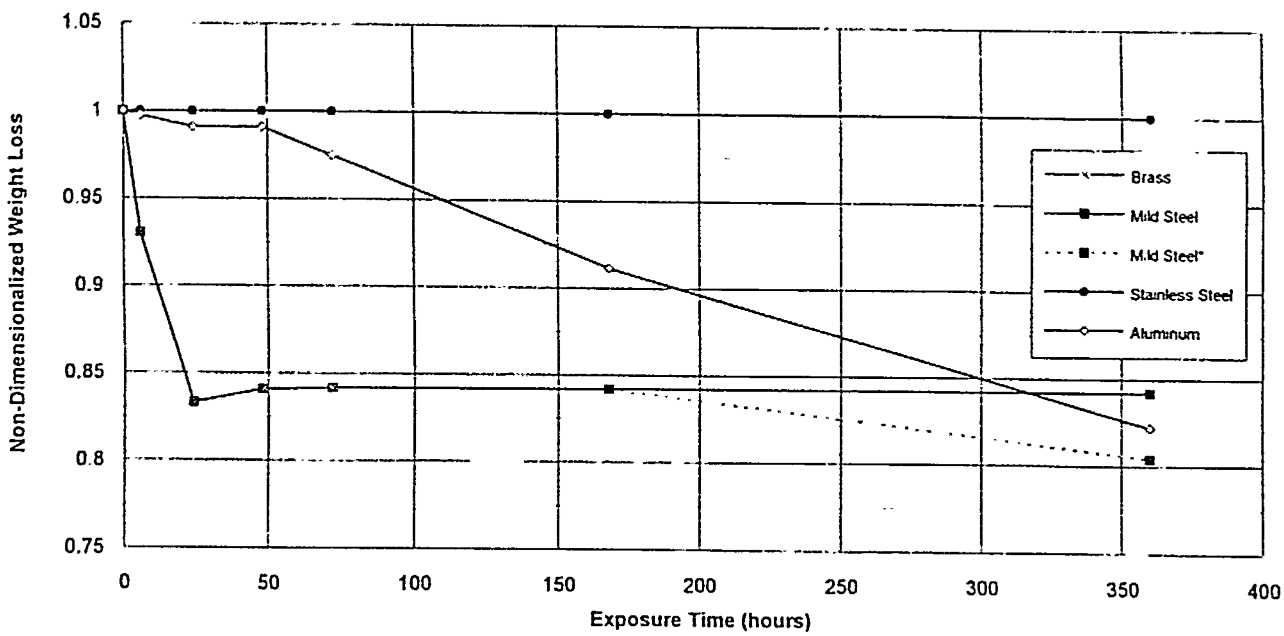


Figure 4: High Temperature (70°C) Corrosion Test Results.

Biomass Pyrolysis Oil Properties and Combustion Meeting

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APPENDIX

R&D ACTIVITIES AT ELKRAFT

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Since the first oil crisis in 1973 a great number of countries have been involved in considerable activities concerning the development of technologies for conversion of biomass into electricity, liquid fuels and chemicals with higher efficiencies. A considerable number have comprised gasification and pyrolysis.

In Denmark, pilot-plant gasification activities were not started until 1986 after the Government decision of local CHP development. The resource distribution led to a decision that ELKRAFT should take care of straw and ELSAM of animal manure. Since 1987 and until the start of the UVE programme of the Danish Energy Agency, ELKRAFT has been engaged in almost all R&D projects aiming at the 1-10 MW_e range.

Many projects continue as independent development projects within ELKRAFT, as a parallel to the joint ELSAM/ELKRAFT action plan. Of these projects it is worth mentioning:

- Acquisition of basic knowledge and development of new processes for straw gasification and, to a less degree, gasification of other types of biomass. In this context a new concept has been developed and is now upscaled with support from the UVE programme at the Laboratory for Energetics, the Technical University of Denmark.

- Design, construction and tests on a 1 MW counter-current straw gasifier located at the Kyndby power station. This includes tests with catalytic gas treatment of a partial flow (succeeding the main flow) and gas engine operation (250 kW).

- Development of a special straw pyrolysis unit. The pyrolytic gas is fired in a separate superheater at a waste-fired CHP station to increase steam data and thus the electricity output without risk of high-temperature corrosion. The concept is now demonstrated in full scale at the Slagelse CHP station. The budget is approx. DKK 21 million.

- Test programme concerning straw flash pyrolysis. The purpose of this project is to examine the possibility of handling and converting straw into pyrolytic oil. Preliminary results show a fairly realistic potential. The tests are carried out in Canada.

- In Finland a project examining the application of biomass-based pyrolysis is carried out. The main purpose is to identify the possibilities of converting the pyrolytic oil in a diesel engine. Today a 60 kW 4-cylinder diesel engine applies the product. The last phase of the project includes tests with a high-efficiency 1 MW diesel engine.

- Development of a Danish Stirling gas engine. The purpose of the project is to develop a 150 kW_e Stirling engine using solid fuel. The expected efficiency of the plant is approx. 30 per cent. Tests on a 12 kW model motor show this process as potentially feasible. The maximum engine size will probably be 1.6 MW_e.

The activities mentioned are coordinated both with the joint action plan and with activities of the Danish Energy Agency under the EFP and UVE programmes.

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This is a bound set of conference papers given in September 1994 that reviewed approaches that have been taken, progress that has been made, and gives some projections for the near and long-term prospects for the commercialization of pyrolysis related activities.

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